

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

APPLICANTS: Mark D. Fokema, Wendall E. Rhine, Neng Ye, Kang P. Lee, and Jennifer P. Gordon  
ASSIGNEE: Aspen Products Group, Inc.  
SERIAL NUMBER: 10/617,912 CONFIRMATION No.: 4220  
FOR: Methods and Compositions for Desulfurization of Hydrocarbon Fuels

Boston, Massachusetts

**Appeal Brief**

Pursuant to 35 U.S.C. §134(a) and 37 C.F.R. 1.192, applicants appeal the final rejection of the pending claims of the above-identified patent application. In the final Office Action of July 14, 2006, pending claims 1-15, 17-34 and 36 were finally rejected under 34 U.S.C. §103(a). A Notice of Appeal was timely filed on October 13, 2006. Payment in the amount of \$250.00 is made to cover the fee for filing a brief in support of an appeal pursuant to 37. C.F.R. 41.20(b)(2) and in the amount of \$60.00 is made to cover the petition fee for a one-month extension of time pursuant to 37 C.F.R. § 1.17(a)(1). With the extension, this appeal brief is due January 16, 2006. The Commissioner is hereby authorized to charge any additional fees that may be due, or credit any overpayment of same, to Deposit Account No. 50-0311, Reference No. 26048-013.

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**Real Party in Interest**

The real party in interest for this brief is Aspen Products Group, Inc., by way of assignments from the inventors, which were recorded at the United States Patent and Trademark Office at Reel 014284, Frame 0449, on July 11, 2003, and at Reel 017092, Frame 0681, on October 14, 2005.

### **Related Appeals and Interferences**

None.



**Status of Claims**

Claims 1-15, 17-34 and 36 are rejected and subject to this appeal. Claim 35 is withdrawn as non-elected after a restriction.

**Status of Amendments**

No claim amendments were submitted after final rejection, though a Response after Final, with additional arguments, was filed on September 13, 2006. An Advisory Action was issued by the Examiner on September 18, 2006, indicating that the claims remained under rejection.

## Summary of the Claimed Subject Matter

The sole independent claims are claims 1 and 28.

Claim 1 recites the following:

A process for removing sulfur from a sulfur-containing hydrocarbon fuel comprising:

- a) contacting a hydrocarbon fuel in the absence of added hydrogen at a temperature in the range of 350 to 600°C and at a pressure in the range from about 790 kPa to about 3.5 MPa with a primary desulfurization agent (support at: claims 1 and 28, as originally filed; page 5, lines 3-4 and 16-21; page 6, lines 25-30; page 8, lines 5-9; and page 21, lines 4-7)
- b) in the form of a metal oxide selected from the group consisting of molybdenum oxide, tantalum oxide, tungsten oxide and combinations thereof (support at: claim 33, as originally filed; page 5, lines 13-14; page 8, line 24, through page 9, line 26; page 13, lines 6-16; and page 21, lines 7-8)
- c) to produce a reaction between the hydrocarbon fuel and the primary desulfurization agent that removes sulfur from the hydrocarbon fuel by replacing oxygen in the metal oxide with the sulfur from the hydrocarbon fuel to form a metal sulfide (support at: claim 28, as originally filed; page 8, lines 24-28; and page 9, lines 6 and 7); and
- d) regenerating the primary desulfurization agent by exposing it to oxygen at a temperature in the range of 350 to 600°C to replace the sulfur in the metal sulfide with oxygen to revert back to the metal oxide (support at: claims 1 and 28, as originally filed; page 5, lines 7-12; page 8, lines 9-11 and 27-28; and page 9, line 10).

Claim 28 recites the following:

A process for removing sulfur from a sulfur-containing hydrocarbon fuel comprising:

- a) contacting a hydrocarbon fuel in the absence of added hydrogen with a primary desulfurization agent (support at: claim 28, as originally filed; page 5, lines 3-4 and 19-21; page 6, lines 25-30; and page 21, line 4)
- b) comprising a transition metal oxide selected from the group consisting of molybdenum oxide, tantalum oxide, tungsten oxide and combinations thereof (support at: claim 33, as originally filed; page 5, lines 13-14; page 8, line 24, through page 9, line 26; page 13, lines 6-16; and page 21, lines 7-8),
- c) wherein the primary desulfurization agent removes sulfur from hydrocarbons in the sulfur-containing hydrocarbon fuel via conversion of the transition metal oxide into a transition metal sulfide (support at: claim 28, as originally filed; page 8, lines 24-28; and page 9, lines 6 and 7); and
- d) regenerating the desulfurization agent by exposing it to oxygen to convert the transition metal sulfide back to a transition metal oxide (support at: claim 28, as originally filed; page 5, lines 7-12; page 8, lines 27-28; and page 9, line 10).

## **Grounds of Rejection to be Reviewed on Appeal**

- Whether claims 1, 5, 6, 10-14, 17-34 and 36 are unpatentable under 35 U.S.C. §103(a) over US Patent 6,184,176 (Khare) in view of US Patent 4,464,252 (Eberly, Jr., *et al.*).
- Whether claims 2, 3 and 15 are unpatentable under 35 U.S.C. §103(a) over Khare in view of WO 02/22763.
- Whether claim 4 is unpatentable under 35 U.S.C. §103(a) over Khare in view of WO 02/22763 and US Patent 4,911,823 (Chen *et al.*).
- Whether claims 7 and 8 are unpatentable under 35 U.S.C. §103(a) over Khare in view of US 4,179,361 (Michlmayr).
- Whether claim 9 is unpatentable under 35 U.S.C. § 103(a) over Khare in view of Michlmayr and WO 02/22763.

## Argument

Four distinct techniques are known for removing sulfur from hydrocarbon fuels; these four techniques are described in the Applicants' specification, as follows:

Techniques for the removal of sulfur from hydrocarbon fuels can be divided into the following four general categories: 1) hydrodesulfurization, which can be characterized by the conversion of organically bound sulfur to H<sub>2</sub>S in the presence of hydrogen; 2) cracking, which can be characterized by the conversion of organically bound sulfur to H<sub>2</sub>S; 3) chemical absorption, which can be characterized by the abstraction of sulfur from the fuel at moderate temperature; and 4) physical absorption, which can be characterized by the removal of sulfur-containing compounds from the fuel at low temperature.<sup>1</sup>

The processes of this invention fall within technique #3 (*i.e.*, chemical absorption), utilizing particular metal oxides, and can be practiced as a simple method using a simple set of materials to desulfurize high-molecular-weight hydrocarbon fuels that are traditionally difficult to desulfurize.<sup>2</sup> It has not previously been suggested that these metal oxides (*i.e.*, molybdenum oxide, tantalum oxide, and tungsten oxide) can practically remove sulfur from heavy hydrocarbons in the absence of hydrogen through an absorptive (“absorption” denotes bulk process) or chemically reactive process.

The prolonged ability of these particular metal oxides to extract sulfur from non-reactive molecules, such as dibenzothiophenes,<sup>3</sup> is surprising in that resulting hydrocarbon fragments and coke do not foul the absorbent surface to rapidly degrade sulfur absorbent capability.<sup>4</sup> These fuels have high aromatics concentrations (typically greater than 20% for diesel and jet fuel) that would be expected to further contribute to blockage of active absorption sites by coke formation. Hydrogen would conventionally be co-fed in such a process to reduce the production of coke precursors and assist in gasifying surface carbon deposits<sup>5</sup>; this use of hydrogen in hydrodesulfurization and chemical desulfurization processes with other catalysts and absorbents is well known.

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<sup>1</sup> USSN 10/617,912, page 2, lines 1-7.

<sup>2</sup> *Id.*, page 1, lines 12-29, and page 4, line 27, through page 5, line 5.

<sup>3</sup> *Id.*, page 11, line 11, through page 15, line 2 (*i.e.*, Examples 1-5).

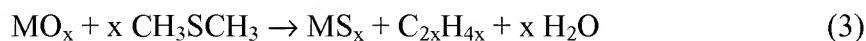
<sup>4</sup> *See, e.g., id.*, page 12, lines 10-11.

<sup>5</sup> *See, e.g., id.*, page 2, lines 12-14, 18-21 and 30-31.

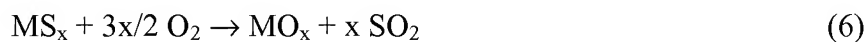
It is also surprising that the transformation of molybdenum oxide into molybdenum sulfide can occur in the absence of added hydrogen, as the molybdenum oxidation state must be reduced from six to four (*i.e.*,  $\text{Mo}^{+6}\text{O}^{-2}_3$  to  $\text{Mo}^{+4}\text{S}^{-2}_2$ ) in this process. Hydrogen is commonly blended with  $\text{H}_2\text{S}$  to convert Ni-Mo oxides to Ni-Mo sulfides during the presulfidization step associated with the use of molybdenum-based hydrodesulfurization catalysts.<sup>6</sup> In the current process, fuel species are apparently sufficiently strong reducing agents to assist in the reduction of molybdenum from an oxidation state of six to four during the desulfurization reaction.

More specifically (and as outlined in the above summary of claimed subject matter), each of the independent claims (*i.e.*, claims 1 and 28) is directed to a process for removing sulfur from a hydrocarbon fuel, wherein the hydrocarbon fuel is contacted with a primary desulfurization agent ***in the absence of added hydrogen***; wherein the primary desulfurization agent includes one or more of the following metal oxides: ***molybdenum oxide, tantalum oxide and/or tungsten oxide***, wherein the sulfur is removed from the hydrocarbon fuel by ***converting the metal oxide into a metal sulfide***; and wherein the desulfurization agent is regenerated by ***converting the metal sulfide back to the metal oxide***.

This chemical-absorption technique is exemplified by the following typical reactions, set forth in the specification,<sup>7</sup> with “M” representing the transitional metal species:



Meanwhile, the following example reaction for regeneration is characterized in the specification<sup>8</sup> as follows:



The three absorbents identified for use in this chemical-absorption technique in claim 1 exhibited superior performance for removing sulfur via chemical bonding, as evidenced by the following table, presented as “Table 2” in the specification<sup>9</sup>:

<sup>6</sup> See, *e.g.*, WO 02/22763, page 20, last sentence of the first full paragraph.

<sup>7</sup> USSN 10/617,912, page 9, lines 4-7.

<sup>8</sup> *Id.*, page 9, lines 9-10.

<sup>9</sup> *Id.*, page 13, lines 13-19.

Absorbent	Sulfur Removal (%)
19 wt% MoO <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	65
29 wt% Ta <sub>2</sub> O <sub>5</sub> /Al <sub>2</sub> O <sub>3</sub>	35
22 wt% WO <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	31
16 wt% ZnTiO <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	28
21 wt% ZnO/Al <sub>2</sub> O <sub>3</sub>	11
11 wt% MnO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	8

None of the cited references, alone or in combination, suggest that oxides of molybdenum, tantalum, and tungsten can produce superior results in terms of sulfur removal, such as the results evidenced in the above table, via chemical absorption in the absence of added hydrogen. Consequently, Applicants respectfully submit that the combination of features, cited in the above summary of claimed subject matter (and which is found in all of the pending claims), is non-obvious over the cited references.

To facilitate a comparison of the claimed subject matter with the teachings of the cited references considered most relevant to the independent claims, the chart on the following page compares the above-highlighted combination of elements from the independent claims with the teachings of the cited references:



<b>Claimed Process</b>	<b>absence of added hydrogen</b>	<b>use of molybdenum oxide, tantalum oxide or tungsten oxide in primary desulfurization agent</b>	<b>sulfur-removal mechanism: conversion of metal oxide into metal sulfide</b>	<b>regeneration mechanism: conversion of metal sulfide back to metal oxide</b>
<b>Khare</b>	<b>Teaches away from:</b> discloses substantially better results with the addition of hydrogen during desulfurization <sup>10</sup>	<b>No:</b> discloses an absorbent including reduced-valence cobalt incorporated into a zinc oxide, silica and alumina mixture. <sup>11</sup>	<b>No:</b> sulfur is removed by "substantially zero valence cobalt" <sup>12</sup> ; accordingly the removal mechanism does not involve a metal oxide.	<b>No:</b> a regeneration process is disclosed, <sup>13</sup> but there is no disclosure of the particular metal-sulfide to metal-oxide conversion process.
<b>Eberly, Jr., et al.</b>	"The desulfurization of the naphtha feed is accomplished, either in the absence or presence of added hydrogen. Preferably, hydrogen is not used." <sup>14</sup>	Discloses a catalyst containing Mo, Ni, and V metals/oxides.	<b>No:</b> The background section is directed to hydrodesulfurization catalytic processes, where organically bound sulfur is converted to H <sub>2</sub> S in the presence of hydrogen <sup>15</sup> ; meanwhile, processes that are characterized as "the invention" are carried out at comparatively low temperatures [ <i>i.e.</i> , with a maximum temperature of about 600°F (316°C), preferably from about 300°F to about 500°F], <sup>16</sup> which corresponds with a physical adsorption or absorption technique <sup>17</sup> .	<b>No:</b> there is no disclosure of regenerating to convert a metal sulfide to a metal oxide.
<b>WO 02/22763</b>	<b>Teaches away from:</b> instructs that the addition "of a sufficient amount of hydrogen" is preferred. <sup>18</sup>	<b>Teaches away from:</b> recognizes molybdenum oxide and tungsten oxide as hydrode-sulfurization catalysts, and instructs that the "sorbents . . . are preferably substantially free from active hydrodesulfurization catalysts," including those formed of molybdenum oxide and tungsten oxide, to prevent "substantial conversion of the organic sulfur components in the feedstock into H <sub>2</sub> S by reaction with hydrogen gas." <sup>19</sup>	Discloses the use of sorbents that are converted from a metal oxide to a metal sulfide; 20 suitable active metal oxide sorbents are identified <sup>20</sup> —but not molybdenum oxide, tantalum oxide or tungsten oxide.	Discloses the regeneration of these sorbents with oxygen at an elevated temperature. <sup>21</sup>

<sup>10</sup> Khare, Col. 7, lines 40-49; Col. 10, lines 32-35; and Col. 10, line 64, through Col. 11, line 32 ("When no hydrogen is used in the process . . . , very little reduction in the sulfur content is effected").

<sup>11</sup> *Id.*, Col. 5, line 59, through Col. 6, line 2.

<sup>12</sup> *Id.*, Col. 2, lines 52-58; and Col. 5, line 59, through Col. 6, line 21.

<sup>13</sup> *Id.*, Col. 7, lines 1-3; Col. 8, line 39, through Col. 9, line 18; and Col. 10, lines 36-49.

<sup>14</sup> Eberly, Jr., *et al.*, Col. 2, lines 57-59.

<sup>15</sup> *Id.*, Col. 1, lines 53-57; *see also* the specification of the present application at page 2, line 1-3, and from page 2, line 8, through page 3, line 5, for a discussion of hydrodesulfurization.

<sup>16</sup> *Id.*, Col. 2, lines 48-51.

<sup>17</sup> *See* the specification of the present application (USSN 10/617,912), page 2, lines 6-7, and page 4, lines 21-25, for a discussion of physical absorption.

<sup>18</sup> *Id.*, page 7, first sentence of the first full paragraph.

<sup>19</sup> WO 02/22763, page 20, the two full paragraphs on this page.

<sup>20</sup> *Id.*, page 18, in the sole full paragraph.

<sup>21</sup> WO 02/22763, page 10, last paragraph, to page 11, first paragraph.

As noted by the Examiner,<sup>22</sup> the first of these references, Khare, discloses a sorbent composition that includes zinc oxide, which was found by Applicants to produce considerably inferior results in the chemical absorption experiment reported in Example 3 on page 13 of the present patent application, with the results from Table 2, reproduced above (*i.e.*, the zinc oxide sample removed only 11% of the sulfur, compared with 31%, 35% and 65% for the claimed compounds in the experiment). Moreover, the zinc oxide does not appear to react with sulfur to form zinc sulfide in the process of Khare. Rather, sulfur is removed in the process of Khare by “substantially zero valence cobalt.”<sup>23</sup> Consequently, the sulfur removal process of Khare is not one in which the sulfur from the hydrocarbon fuel is substituted for the oxygen in a metal oxide as specified in Applicants’ amended claims, but rather is one in which a reduced metal bonds to the sulfur.

Second, the Examiner asserted that “Eberly [in the Background section] discloses using molybdenum and tungsten oxides to ‘[c]atalytically remove sulfur from petroleum fractions, crude oils, and other mixtures of hydrocarbons’ (Col. 1, lines 12-20).”<sup>24</sup> The Applicants respectfully disagrees with this characterization because the reference to molybdenum (Mo) and tungsten (W) in this section refers to them as metals (in true practice, metal sulfides), rather than as metal oxides. Moreover, the process described in the Background section of Eberly is a true catalytic hydrodesulfurization process (falling within technique #1 quoted on page 4 of this Brief), wherein sulfur is “catalytically removed in the form of hydrogen sulfide, H<sub>2</sub>S,”<sup>25</sup> rather than involving a metal-oxide to metal-sulfide conversion as specified in Applicants’ claims.

With respect to claim 1, the Examiner further asserted that Eberly discloses a process for removing sulfur from a hydrocarbon using a sorbent containing MoO<sub>3</sub> on alumina and also that the sorbent is used in a process at a temperature with the claimed range of claim 1.<sup>26</sup> Applicant respectfully disagrees with this characterization. The highest temperature range suggested by Eberly is 100°F to 600°F (*i.e.*, 38°C to 316°C).<sup>27</sup> This range corresponds with the low-temperature range for physical adsorption, cited in the quoted text on page 10 of this Brief as

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<sup>22</sup> Office Action of July 14, 2006, page 3.

<sup>23</sup> Khare, Col. 5, line 59, through Col. 6, line 21.

<sup>24</sup> Office Action of July 14, 2006, page 9.

<sup>25</sup> Eberly, Jr., *et al.*, Col. 1, lines 55-57 (see also the “hydrodesulfurize” characterization of the process at Col. 2, lines 5-9 of Eberly, Jr., *et al.*).

<sup>26</sup> Office Action of July 14, 2006, page 5.

<sup>27</sup> *Id.*, Col. 2, lines 48-50.

technique #4, and is below the lower limit of 350°C set forth in claim 1. Moreover, Eberly states that “it is quite possible that the molybdenum is also capable of combining, and hence may in fact *combine with the sulfur compound*”<sup>28</sup> (emphasis added). This description is representative of the physical-adsorption technique (#4), in which the entire sulfur-containing hydrocarbon compound is removed from the fuel stream, rather than the chemical-absorption technique (#3), in which the sulfur atom alone is extracted from the fuel molecule.

The Examiner also noted<sup>29</sup> that WO 02/22763 discloses the use of metal oxides (preferably zinc oxide or iron oxide<sup>30</sup>) to remove sulfur. However, WO 02/22763 teaches away from using compounds of molybdenum and tungsten, which it characterizes as “active hydrodesulfurization catalysts,” in its sorbents by specifying that the sorbents “are preferably substantially free from active hydrodesulfurization catalysts” so as to prevent “substantial conversion of the organic sulfur components into H<sub>2</sub>S by reaction with hydrogen gas.”<sup>31</sup> WO 02/22763 further discloses that “oxides of molybdenum . . . and tungsten can be readily converted to the active sulfides by *exposure to hydrogen* and sulfur compounds in the hydrocarbon feeds . . .” (emphasis added).<sup>32</sup> However, WO 02/22763 offers no suggestion that molybdenum oxide or tungsten oxide can be used in the claimed process *in the absence of added hydrogen* to chemically remove sulfur.

Finally, Chen and Michlmayer, which were cited by the Examiner for particular limitations found in various dependent claims, likewise fail to offer any disclosure or suggestion of using any of the recited metal oxides in a chemical-absorption process to remove sulfur and do not otherwise remedy the deficiencies of the above-discussed references with respect to the independent claims.

With this appeal brief, applicants have addressed and provided reasons for the reversal of the Examiner’s rejection of claims 1-15, 17-34 and 36 under 35 U.S.C. §103(a). In view of the

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<sup>28</sup> *Id.*, Col. 4, lines 4-6.

<sup>29</sup> Office Action of July 14, 2006, pages 5-6.

<sup>30</sup> WO 02/22763, in the paragraph bridging pages 6 and 7.

<sup>31</sup> *Id.*, in the two full paragraphs on page 20.

<sup>32</sup> *Id.*, page 20, last sentence of the first full paragraph.

arguments set forth in this appeal brief, applicants respectfully request reversal of each of the Examiner's rejections and remand of this application for issuance of a Notice of Allowance.

Respectfully submitted,

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## Claims Appendix

1. A process for removing sulfur from a sulfur-containing hydrocarbon fuel comprising:  
    contacting a hydrocarbon fuel in the absence of added hydrogen at a temperature in the range of 350 to 600°C and at a pressure in the range from about 790 kPa to about 3.5 MPa with a primary desulfurization agent in the form of a metal oxide selected from the group consisting of molybdenum oxide, tantalum oxide, tungsten oxide and combinations thereof to produce a reaction between the hydrocarbon fuel and the primary desulfurization agent that removes sulfur from the hydrocarbon fuel by replacing oxygen in the metal oxide with the sulfur from the hydrocarbon fuel to form a metal sulfide; and  
    regenerating the primary desulfurization agent by exposing it to oxygen at a temperature in the range of 350 to 600°C to replace the sulfur in the metal sulfide with oxygen to revert back to the metal oxide.
2. The process of claim 1, further comprising the step of contacting the hydrocarbon fuel with an acidic inorganic material at a temperature in the range of 300 to 600°C and at a pressure in the range of about 790 kPa to about 3.5 MPa to effect a reduction in the average molecular weight of the hydrocarbon fuel.
3. The process of claim 2, wherein the acidic inorganic material is a zeolite.
4. The process of claim 3, wherein the acidic inorganic material is a mixture of H-ZSM-5 and H-Beta zeolites.
5. The process of claim 1, further comprising the step of separating a higher-boiling fraction and a lower-boiling fraction from the hydrocarbon fuel after the hydrocarbon fuel contacts the primary desulfurization agent.
6. The process of claim 5, wherein the higher-boiling fraction and lower-boiling fraction are separated at a temperature in the range of 200 to 400°C and at a pressure in the range from about 100 kPa to about 2.9 MPa.

7. The process of claim 5, further comprising the step of contacting the lower-boiling fraction with a secondary desulfurization agent.
8. The process of claim 7, wherein the secondary desulfurization agent is a metal or metal oxide absorbent.
9. The process of claim 8, wherein the secondary desulfurization agent is Ni/Al<sub>2</sub>O<sub>3</sub> or Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>.
10. The process of claim 5, wherein the higher-boiling fraction derived is combusted to provide heat that is transported to the primary desulfurization agent.
11. The process of claim 5, wherein the higher-boiling fraction is recycled and passed through the desulfurization system a second time.
12. The process of claim 1, wherein the hydrocarbon fuel comprises gasoline, kerosene, diesel fuel, jet fuel, heating oil or combinations thereof.
13. The process of claim 1, wherein the hydrocarbon fuel includes sulfur at a concentration greater than 100 parts per million by weight.
14. The process of claim 1, wherein the hydrocarbon fuel contacts the primary desulfurization agent at a pressure in the range from about 1.5 MPa to about 2.5 MPa and at a temperature in the range of 350°C to 475°C.
15. The process of claim 1, wherein organosulfur compounds in the hydrocarbon fuel are cracked to produce H<sub>2</sub>S and cracked hydrocarbon products before or while the hydrocarbon fuel contacts the primary desulfurization agent.
17. The process of claim 1, wherein the metal oxide is supported on an inorganic support.

18. The process of claim 1, wherein the metal in the metal oxide is selected from the group of elements consisting of Mo, W, and mixtures thereof, and wherein the metal oxide is supported on an inorganic support.
19. The process of claim 1, wherein the primary desulfurization agent comprises MoO<sub>3</sub>.
20. The process of claim 19, wherein the MoO<sub>3</sub> is coated on an Al<sub>2</sub>O<sub>3</sub> substrate.
21. The process of claim 20, wherein the primary desulfurization agent comprises:  
15-30 weight-% MoO<sub>3</sub>; and  
70-85 weight-% of a combination of Al<sub>2</sub>O<sub>3</sub> and another transition metal species.
22. The process of claim 20, wherein the primary desulfurization agent is 15-30 weight-% MoO<sub>3</sub> and 70-85 weight-% Al<sub>2</sub>O<sub>3</sub>.
23. The process of claim 19, wherein the primary desulfurization agent comprises at least about 90% MoO<sub>3</sub>.
24. The process of claim 1, wherein the primary desulfurization agent is regenerated by exposing it to oxygen at 350 to 475°C.
25. The process of claim 1, wherein the primary desulfurization agent is regenerated by exposing it to oxygen at a temperature that is substantially the same as that at which the primary desulfurization agent removes sulfur from the hydrocarbon fuel.
26. The process of claim 1, wherein in the reaction between the hydrocarbon fuel and the primary desulfurization agent, the primary desulfurization agent abstracts sulfur from the hydrocarbon fuel.
27. The process of claim 1, wherein the amount of at least one of dibenzothiophene, alkyl dibenzothiophene compounds and dialkyl dibenzothiophene compounds in the hydrocarbon fuel is reduced by the process.

28. A process for removing sulfur from a sulfur-containing hydrocarbon fuel comprising:  
contacting a hydrocarbon fuel in the absence of added hydrogen with a primary desulfurization agent comprising a transition metal oxide selected from the group consisting of molybdenum oxide, tantalum oxide, tungsten oxide and combinations thereof, wherein the primary desulfurization agent removes sulfur from hydrocarbons in the sulfur-containing hydrocarbon fuel via conversion of the transition metal oxide into a transition metal sulfide; and  
regenerating the desulfurization agent by exposing it to oxygen to convert the transition metal sulfide back to a transition metal oxide.
29. The process of claim 28, wherein the conversion of the transition metal oxide into a transition metal sulfide and the conversion of the transition metal sulfide back into a transition metal oxide each occur at a temperature in the range from 350 to 600°C.
30. The process of claim 28, wherein the conversion of the transition metal oxide into a transition metal sulfide and the conversion of the transition metal sulfide back into a transition metal oxide each occur at a temperature in the range from 350 to 475°C.
31. The process of claim 28, wherein the hydrocarbons from which the sulfur is removed comprise at least one of dibenzothiophene, alkyldibenzothiophene compounds, and dialkylbenzothiophene compounds.
32. The process of claim 28, wherein the conversion of the transition metal oxide into a transition metal sulfide and the conversion of the transition metal sulfide back into a transition metal oxide each occur at substantially the same temperature.
33. The process of claim 28, wherein the transition metal oxide comprises a metal oxide selected from the group consisting of  $\text{MoO}_3$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{WO}_3$  and combinations thereof.
34. The process of claim 28, wherein the metal oxide is  $\text{MoO}_3$ .
36. The process of claim 28, wherein the metal oxide is supported on an inorganic support.



## Evidence Appendix

The following references, which were cited by the Examiner in rejecting claims under 35 U.S.C. §103(a), are provided, starting on the following pages:

<b>Page</b>	<b>Reference</b>
22	U.S. 6,184,176 (Khare)
29	U.S. 4,464,252 (Eberly, Jr., <i>et al.</i> )
32	WO 02/22763 A1
86	US 4,911,823 (Chen <i>et al.</i> )
97	US 4,179,361 (Michlmayr)



US006184176B1

(12) **United States Patent**  
**Khare**

(10) **Patent No.:** **US 6,184,176 B1**  
(45) **Date of Patent:** **Feb. 6, 2001**

(54) **PROCESS FOR THE PRODUCTION OF A  
SULFUR SORBENT**

5,710,089 \* 1/1998 Khare .

5,985,169 \* 11/1999 Miller et al. .

(75) Inventor: **Gyanesh P. Khare**, Bartlesville, OK  
(US)

\* cited by examiner

(73) Assignee: **Phillips Petroleum Company**,  
Bartlesville, OK (US)

*Primary Examiner*—Steven P. Griffin

*Assistant Examiner*—Christina Ildebrando

(\*) Notice: Under 35 U.S.C. 154(b), the term of this  
patent shall be extended for 0 days.

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(57) **ABSTRACT**

(21) Appl. No.: **09/382,502**

(22) Filed: **Aug. 25, 1999**

(51) **Int. Cl.**<sup>7</sup> ..... **B01J 20/00**; B01J 20/08;  
B01J 20/10

(52) **U.S. Cl.** ..... **502/407**; 502/415; 502/325;  
502/329; 502/343

(58) **Field of Search** ..... 502/400, 407,  
502/414, 415, 325, 329, 343

(56) **References Cited**

U.S. PATENT DOCUMENTS

4,826,800 \* 5/1989 McAteer .

Particulate sorbent compositions comprising a mixture of zinc oxide, silica, alumina and a substantially reduced valence cobalt are provided for the desulfurization of a feedstream of cracked-gasoline or diesel fuels in a desulfurization zone by a process which comprises the contacting of such feedstreams in a desulfurization zone followed by separation of the resulting low sulfur-containing stream and sulfurized-sorbent and thereafter regenerating and activating the separated sorbent before recycle of same to the desulfurization zone.

**11 Claims, No Drawings**

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## PROCESS FOR THE PRODUCTION OF A SULFUR SORBENT

### FIELD OF THE INVENTION

This invention relates to the removal of sulfur from fluid streams of cracked-gasolines and diesel fuels. In another aspect this invention relates to sorbent compositions suitable for use in the desulfurization of fluid streams of cracked-gasolines and diesel fuel. A further aspect of this invention relates to a process for the production of sulfur sorbents for use in the removal of sulfur bodies from fluid streams of cracked gasolines and diesel fuels.

### BACKGROUND OF THE INVENTION

The need for cleaner burning fuels has resulted in a continuing world wide effort to reduce sulfur levels in gasoline and diesel fuels. The reducing of gasoline and diesel sulfur is considered to be a means for improving air quality because of the negative impact the fuel sulfur has on the performance of automotive catalytic converters. The presence of oxides of sulfur in automotive engine exhaust inhibits and may irreversibly poison noble metal catalysts in the converter. Emissions from an inefficient or poisoned converter contain levels of non-combusted, non-methane hydrocarbon and oxides of nitrogen and carbon monoxide. Such emissions are catalyzed by sunlight to form ground level ozone, more commonly referred to as smog.

Most of the sulfur in gasoline comes from the thermally processed gasolines. Thermally processed gasolines such, as for example, thermally cracked gasoline, visbreaker gasoline, coker gasoline and catalytically cracked gasoline (hereinafter collectively called "cracked-gasoline") contains in part olefins, aromatics, and sulfur-containing compounds.

Since most gasolines, such as for example automobile gasolines, racing gasolines, aviation gasoline and boat gasolines contain a blend of at least in part cracked-gasoline, reduction of sulfur in cracked-gasoline will inherently serve to reduce the sulfur levels in such gasolines.

The public discussion about gasoline sulfur has not centered on whether or not sulfur levels should be reduced. A consensus has emerged that lower sulfur gasoline reduces automotive emissions and improves air quality. Thus the real debate has focused on the required level of reduction, the geographical areas in need of lower sulfur gasoline and the time frame for implementation.

As the concern over the impact of automotive air pollution continues, it is clear that further efforts to reduce the sulfur levels in automotive fuels will be required. While the current gasoline products contain about 330 part per million with continued efforts by the Environmental Protection Agency to secure reduced levels, it has been estimated that gasoline will have to have less than 50 part per million of sulfur by the year 2010. (See Rock, K. L., Putman H. M., Improvements in FCC Gasoline Desulfurization via Catalytic Distillation" presented at the 1998 National Petroleum Refiners Association Annual Meeting (AM-98-37)).

In view of the ever increasing need to be able to produce a low sulfur content automotive fuel, a variety of processes have been proposed for achieving industry compliance with the Federal mandates.

One such process which has been proposed for the removal of sulfur from gasoline is called hydrodesulfurization. While hydrodesulfurization of gasoline can remove sulfur-containing compounds, it can result in the saturation of most, if not all, of the olefins contained in the gasoline.

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This saturation of olefins greatly affects the octane number (both the research and motor octane number) by lowering it. These olefins are saturated due to, in part, the hydrodesulfurization conditions required to remove thiophenic compounds (such as, for example, thiophene, benzothiophene, alkyl thiophenes, alkylbenzothiophenes and alkyl dibenzothiophenes), which are some of the most difficult sulfur-containing compounds to removed. Additionally, the hydrodesulfurization conditions required to remove thiophenic compounds can also saturate aromatics.

In addition to the need for removal of sulfur from cracked-gasolines, there is also presented to the petroleum industry a need to reduce the sulfur content of diesel fuels. In removing sulfur from diesel by hydrodesulfurization, the cetane is improved but there is a large cost in hydrogen consumption. This hydrogen is consumed by both hydrodesulfurization and aromatic hydrogenation reactions.

Thus there is a need for a process wherein desulfurization without hydrogenation of aromatics is achieved so as to provide a more economical process for the treatment of diesel fuels.

As a result of the lack of success in providing successful and economically feasible process for the reduction of sulfur levels in both cracked-gasolines and diesel fuels, it is apparent that there is still needed a better process for the desulfurization of both cracked-gasolines and diesel fuels which has minimal affect of octane while achieving high levels of sulfur removal.

It is thus an object of the present invention to provide a novel sorbent system for the removal of sulfur from fluid streams of cracked-gasolines and diesel fuels.

Another object of this invention is to provide a process for the production of novel sorbents which are useful in the desulfurization of such fluid streams.

Another object of this invention is to provide a process for the removal of sulfur-containing compounds from cracked-gasolines and diesel fuels which minimize saturation of olefins and aromatics therein.

A still further object of this invention is to provide a desulfurized cracked-gasoline that contains less than about 100 parts per million of sulfur based on the weight of the desulfurized cracked-gasoline and which contains essentially the same amount of olefins and aromatics as were in the cracked-gasoline from which it is made.

Other aspects, objects and the several advantages of this invention will be apparent from the following description of the invention and the appended claims.

### SUMMARY OF THE INVENTION

The present invention is based upon our discovery that through the utilization of cobalt in a substantially reduced valence state, preferably zero, in a sorbent composition there is achieved a novel sorbent composition which permits the ready removal of sulfur from streams of cracked-gasolines or diesel fuels with a minimal effect on the octane rating of the treated stream.

Accordingly, in one aspect of the present invention there is provided a novel sorbent suitable for the desulfurization of cracked-gasolines or diesel fuels which is comprised of zinc oxide, silica, alumina and cobalt wherein the valence of the cobalt is substantially reduced and such reduced valence cobalt is present in an amount to permit the removal of sulfur from cracked-gasolines or diesel fuels.

In accordance with another aspect of the present invention, there is provided a process for the preparation of

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a novel sorbent composition which comprises admixing zinc oxide, silica and alumina so as to form a wet mix, dough, paste or slurry thereof, particulating the wet mix, dough, paste or slurry thereof so as to form a particulate granule, extrudate, tablet, sphere, pellet or microsphere thereof; drying the resulting particulate; calcining the dried particulate; impregnating the resulting solid particulate with a cobalt or a cobalt-containing compound; drying the resulting impregnated solid particulate composition, calcining the dried particulate composition and reducing the calcined product with a suitable reducing agent, such as hydrogen, so as to produce a sorbent composition having a substantial zero valence cobalt content in an amount which is sufficient to permit the removal with same of sulfur from a cracked-gasoline or diesel fuel stream.

In accordance with a further aspect of the present invention, there is provided a process for the desulfurization of a cracked-gasoline or diesel fuel stream which comprises desulfurizing in a desulfurization zone a cracked-gasoline or diesel fuel with a solid-reduced cobalt metal-containing sorbent, separating the desulfurized cracked-gasoline or diesel fuel from the sulfurized sorbent, regenerating at least a portion of the sulfurized-solid-reduced cobalt metal metal-containing sorbent to produce a regenerated desulfurized solid cobalt metal metal-containing sorbent; activating at least a portion of the regenerated desulfurized solid cobalt metal metal-containing sorbent to produce a solid reduced cobalt metal metal-containing sorbent; and thereafter returning at least a portion of the resulting reduced cobalt metal-containing sorbent to the desulfurization zone.

#### DETAILED DESCRIPTION OF THE INVENTION

The term "gasoline" as employed herein is intended to mean a mixture of hydrocarbons boiling from about 100° F. to approximately 400° F. or any fraction thereof. Such hydrocarbons will include, for example, hydrocarbon streams in refineries such as naphtha, straight-run naphtha, coker naphtha, catalytic gasoline, visbreaker naphtha, alkylate, isomerate or reformate.

The term "cracked-gasoline" as employed herein is intended to mean hydrocarbons boiling from about 100° F. to approximately 400° F. or any fraction thereof that are products from either thermal or catalytic processes that crack larger hydrocarbon molecules into smaller molecules. Examples of thermal processes include coking, thermal cracking and visbreaking. Fluid catalytic cracking and heavy oil cracking are examples of catalytic cracking. In some instances the cracked-gasoline may be fractionated and/or hydrotreated prior to desulfurization when used as a feed in the practice of this invention.

The term "diesel fuel" as employed herein is intended to mean a fluid composed of a mixture of hydrocarbons boiling from about 300° F. to approximately 750° F. or any fraction thereof. Such hydrocarbon streams include light cycle oil, kerosene, jet fuel, straight-run diesel and hydrotreated diesel.

The term "sulfur" as employed herein is intended to mean those organosulfur compounds such as mercaptans or those thiophenic compounds normally present in cracked gasolines which include among others thiophene, benzothiophene, alkyl thiophenes, alkyl benzothiophenes and alkyldibenzothiophenes as well as the heavier molecular weights of same which are normally present in a diesel fuel of the types contemplated for processing in accordance with the present invention.

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The term "gaseous" as employed herein is intended to mean that state in which the feed cracked-gasoline or diesel fuel is primarily in a vapor phase.

The term "substantially reduced cobalt valence" as employed herein is intended to mean that a large portion of the valence of the cobalt component of the composition is reduced to a value of less than 3, preferably zero.

The present invention is based upon the discovery of applicants that a substantially reduced valence cobalt component in a particulate composition comprising zinc oxide, silica, alumina and cobalt results in a sorbent which permits the removal of thiophenic sulfur compounds from fluid streams of cracked-gasolines or diesel fuels without having a significant adverse affect of the olefin content of such streams, thus avoiding a significant reduction of octane values of the treated stream. Moreover, the use of such novel sorbents results in a significant reduction of the sulfur content of the resulting treated fluid stream.

In a presently preferred embodiment of this invention, the sorbent composition has a cobalt content in the range of from about 5 to about 50 weight percent.

The zinc oxide used in the preparation of the sorbent composition can either be in the form of zinc oxide, or in the form of one or more zinc compounds that are convertible to zinc oxide under the conditions of preparation described herein. Examples of such zinc compounds include, but are not limited to, zinc sulfide, zinc sulfate, zinc hydroxide, zinc carbonate, zinc acetate, and zinc nitrate. Preferably, the zinc oxide is in the form of powdered zinc oxide.

The silica used in the preparation of the sorbent compositions may be either in the form of silica or in the form of one or more silicon-containing compounds. Any suitable type of silica may be employed in the sorbent compositions of the present invention. Examples of suitable types of silica include diatomite, silicalite, silica colloid, flame-hydrolyzed silica, hydrolyzed silica, silica gel and precipitated silica, with diatomite being presently preferred. In addition, silicon compounds that are convertible to silica such as silicic acid, sodium silicate and ammonium silicate can also be employed. Preferably, the silica is in the form of diatomite.

The starting alumina component of the composition can be any suitable commercially available alumina material including colloidal alumina solutions and, generally, those alumina compounds produced by the dehydration of alumina hydrates.

The zinc oxide will generally be present in the sorbent composition in an amount in the range of from about 10 weight percent to about 90 weight percent, and preferably in an amount in the range of from about 15 to about 60 weight percent when such weight percents are expressed in terms of the zinc oxide based upon the total weight of the sorbent composition.

The silica will generally be present in the sorbent composition in an amount in the range of from about 5 weight percent to about 85 weight percent, preferably in an amount in the range of from about 20 weight percent to about 60 weight percent when the weight percents are expressed in terms of the silica based upon the total weight of the sorbent composition.

The alumina will generally be present in the sorbent composition in an amount in the range of from about 5.0 weight percent to about 30 weight percent, preferably from about 5.0 weight percent to about 15 weight percent when such weight percents are expressed in terms of the weight of the alumina compared with the total weight of the sorbent system.

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In the manufacture of the sorbent composition, the primary components of zinc oxide, silica and alumina are combined together in appropriate proportions by any suitable manner which provides for the intimate mixing of the components to provide a substantially homogeneous mixture.

Any suitable means for mixing the sorbent components can be used to achieve the desired dispersion of the materials. Such means include, among others, tumblers, stationary shells or troughs, Muller mixers, which are of the batch or continuous type, impact mixers and the like. It is presently preferred to use a Muller mixer in the mixing of the silica, alumina and zinc oxide components.

Once the sorbent components are properly mixed to provide a shapeable mixture, the resulting mixture can be in the form of wet mix, dough, paste or slurry. If the resulting mix is in the form of a wet mix, the wet mix can be densified and thereafter particulated through the granulation of the densified mix following the drying and calcination of same. When the admixture of zinc oxide, silica and alumina results in a form of the mixture which is either in a dough state or paste state, the mix can be shaped to form a particulate granule, extrudate, tablet, sphere, pellet or microsphere. Presently preferred are cylindrical extrudates having from  $\frac{1}{32}$  inch to  $\frac{1}{2}$  inch diameter and any suitable length. The resulting particulate is then dried and then calcined. When the mix is in the form of a slurry, the particulation of same is achieved by spray drying the slurry to form micro-spheres thereof having a size of from about 20 to about 500 microns. Such microspheres are then subjected to drying and calcination. Following the drying and calcination of the particulated mixture, the resulting particulates can be impregnated with cobalt oxide compound or a cobalt oxide precursor.

Following the impregnation of the particulate compositions with the appropriate cobalt compound, the resulting impregnated particulate is then subjected to drying and calcination prior to the subjecting of the calcined particulate to reduction with a reducing agent, preferably hydrogen.

The elemental cobalt, cobalt oxide or cobalt-containing compound can be added to the particulated mixture by impregnation of the mixture with a solution, either aqueous or organic, that contains the elemental cobalt, cobalt oxide or cobalt-containing compound. In general, the impregnation with the cobalt is carried out so as to form a resulting particulate composition of zinc oxide, silica, alumina and the cobalt metal, cobalt oxide or cobalt oxide precursor prior to the drying and calcination of the resulting impregnated composition.

The impregnation solution is any aqueous solution and amounts of such solution which suitably provides for the impregnation of the mixture of zinc oxide, silica and alumina to give an amount of cobalt oxide in the final zinc oxide based composition to provide when reduced a reduced cobalt metal content sufficient to permit the removal of sulfur from streams of cracked-gasoline or diesel fuels when so treated with same in accordance with the process of the present invention.

Once the cobalt, cobalt oxide or cobalt oxide precursor has been incorporated into the particulate calcined zinc oxide, alumina and silica mixture, the desired reduced valence cobalt metal sorbent is prepared by drying the resulting composition followed by calcination and thereafter subjecting the resulting calcined composition to reduction with a suitable reducing agent, preferably hydrogen, so as to produce a composition having a substantial zero valence cobalt content therein with such zero valence cobalt content

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being present in an amount to permit the removal with same of sulfur from a cracked-gasoline or diesel fuel fluid stream.

The solid reduced cobalt metal sorbent of this invention is a composition that has the ability to react with and/or chemisorb with organo-sulfur compounds, such as thiophenic compounds. It is also preferable that the sorbent removes diolefins and other gum forming compounds from the cracked-gasoline.

The solid reduced metal sorbent of this invention is comprised of cobalt that is in a substantially reduced valence state, preferably a zero valence state. Presently the reduced metal is cobalt. The amount of reduced cobalt in the solid cobalt reduced metal sorbents of this invention is that amount which will permit the removal of sulfur from a cracked-gasoline or diesel fuel fluid stream. Such amounts are generally in the range of from about 5 to about 50 weight percent of the total weight of cobalt in the sorbent composition. Presently it is preferred that the reduced cobalt metal be present in an amount in the range of from about 15 to about 40 weight percent of the total weight of cobalt in the sorbent composition.

In one presently preferred embodiment of the present invention, the reduced cobalt is present in an amount in the range of from about 15 to 30 weight percent and the cobalt component has been substantially reduced to zero valence.

In another presently preferred embodiment of this invention, zinc oxide is present in an amount of about 38 weight percent, silica is present in an amount of about 31 weight percent, alumina is present in an amount of about 8 weight percent and cobalt is present prior to reduction to zero valence in an amount of about 33 weight percent cobalt oxide.

From the above, it can be appreciated that the sorbent compositions which are useful in the desulfurization process of this invention can be prepared by a process which comprises:

- (a) admixing zinc oxide, silica and alumina so as to form a mix of same in the form of one of a wet mix, dough, paste or slurry;
- (b) particulating the resulting mix to form particulates thereof in the form of one of granules, extrudates, tablets, pellets, spheres or microspheres;
- (c) drying the resulting particulate;
- (d) calcining the dried particulate;
- (e) impregnating the resulting calcined particulate with cobalt, cobalt oxide or a precursor for cobalt;
- (f) drying the impregnated particulate;
- (g) calcining the resulting dried particulate; and
- (h) reducing the calcined particulate product of (g) with a suitable reducing agent so as to produce a particulate composition having a substantial reduced valence cobalt content therein and wherein the reduced valence cobalt content is present in an amount sufficient to permit the removal with same of sulfur from a cracked-gasoline or diesel fuel fluid stream when contacted with the resulting substantially reduced valence cobalt particulated sorbent.

The process to use the novel sorbents to desulfurize cracked-gasoline or diesel fuels to provide a desulfurized cracked-gasoline or diesel fuel comprises:

- (a) desulfurizing in a desulfurization zone a cracked-gasoline or diesel fuel with a solid reduced cobalt metal-containing sorbent;
- (b) separating the desulfurized cracked-gasoline or desulfurized diesel fuel from the resulting sulfurized solid reduced cobalt-containing sorbent;

- (c) regenerating at least a portion of the sulfurized solid reduced cobalt-containing sorbent to produce a regenerated desulfurized solid cobalt-containing sorbent;
- (d) reducing at least a portion of the regenerated desulfurized solid cobalt-containing sorbent to produce a solid reduced cobalt-containing sorbent thereafter and;
- (e) returning at least a portion of the regenerated solid reduced cobalt-containing sorbent to the desulfurization zone.

The desulfurization step (a) of the present invention is carried out under a set of conditions that includes total pressure, temperature, weight hourly space velocity and hydrogen flow. These conditions are such that the solid reduced cobalt-containing sorbent can desulfurize the cracked-gasoline or diesel fuel to produce a desulfurized cracked-gasoline or desulfurized diesel fuel and a sulfurized sorbent.

In carrying out the desulfurization step of the process of the present invention, it is preferred that the feed cracked-gasoline or diesel fuel be in a vapor phase. However, in the practice of the invention it is not essential, albeit preferred, that the feed be totally in a vapor or gaseous state.

The total pressure can be in the range of about 15 psia to about 1500 psia. However, it is presently preferred that the total pressure be in a range of from about 50 psia to about 500 psia.

In general, the temperature should be sufficient to keep the cracked-gasoline or diesel fuel essentially in a vapor phase. While such temperatures can be in the range of from about 100° F. to about 1000° F., it is presently preferred that the temperature be in the range of from about 400° F. to about 800° F. when treating as cracked-gasoline and in the range of from about 500° F. to about 900° F. when the feed is a diesel fuel.

Weight hourly space velocity (WHSV) is defined as the pounds of hydrocarbon feed per pound of sorbent in the desulfurization zone per hour. In the practice of the present invention, such WHSV should be in the range of from about 0.5 to about 50, preferably about 1 to about 20 hr<sup>-1</sup>.

In carrying out the desulfurization step, it is presently preferred that an agent be employed which interferes with any possible chemisorbing or reacting of the olefinic and aromatic compounds in the fluids which are being treated with the solid reduced cobalt-containing sorbent. Such an agent is presently preferred to be hydrogen.

Hydrogen flow in the desulfurization zone is generally such that the mole ratio of hydrogen to hydrocarbon feed is in the range of about 0.1 to about 10, and preferably in the range of about 0.2 to about 3.0.

The desulfurization zone can be any zone wherein desulfurization of the feed cracked-gasoline or diesel fuel can take place. Examples of suitable zones are fixed bed reactors, moving bed reactors, fluidized bed reactors and transport reactors. Presently, a fluidized bed reactor or a fixed bed reactor is preferred.

If desired, during the desulfurization of the vaporized fluids, diluents such as methane, carbon dioxide, flue gas, and nitrogen can be used. Thus it is not essential to the practice of the process of the present invention that a high purity hydrogen be employed in achieving the desired desulfurization of the cracked-gasoline or diesel fuel.

It is presently preferred when utilizing a fluidized system that a solid reduced cobalt sorbent be used that has a particle size in the range of about 20 to about 1000 micrometers. Preferably, such sorbents should have a particle size of from about 40 to about 500 micrometers. When a fixed bed system is employed for the practice of the desulfurization process of

this invention, the sorbent should be such as to have a particle size in the range of about 1/32 inch to about 1/2 inch diameter.

It is further presently preferred to use solid reduced cobalt sorbents that have a surface area of from about 1 square meter per gram to about 1000 square meters per gram of solid sorbent.

The separation of the gaseous or vaporized desulfurized fluids and sulfurized sorbent can be accomplished by any means known in the art that can separate a solid from a gas. Examples of such means are cyclonic devices, settling chambers or other impingement devices for separating solids and gases. The desulfurized gaseous cracked-gasoline or desulfurized diesel fuel can then be recovered and preferably liquefied.

The gaseous cracked-gasoline or gaseous diesel fuel is a composition that contains in part, olefins, aromatics and sulfur-containing compounds as well as paraffins and naphthenes.

The amount of olefins in gaseous cracked-gasoline is generally in the range of from about 10 to 35 weight percent based on the weight of the gaseous cracked-gasoline. For diesel fuel there is essentially no olefin content.

The amount of aromatics in gaseous cracked-gasoline is generally in the range of about 20 to about 40 weight percent based on the weight of the gaseous cracked gasoline. The amount of aromatics in gaseous diesel fuel is generally in the range of about 10 to about 90 weight percent.

The amount of sulfur in cracked-gasolines or diesel fuels can range from about 100 parts per million sulfur by weight of the gaseous cracked-gasoline to about 10,000 parts per million sulfur by weight of the gaseous cracked-gasoline and from about 100 parts per million to about 50,000 parts per million for diesel fuel prior to the treatment of such fluids with the sorbent system of the present invention.

The amount of sulfur in cracked-gasolines or in diesel fuels following treatment of same in accordance with the desulfurization process of this invention is less than 100 parts per million.

In carrying out the process of this invention, if desired, a stripper unit can be inserted before the regenerator for regeneration of the sulfurized sorbent which will serve to remove a portion, preferably all, of any hydrocarbons from the sulfurized sorbent or before the hydrogen reduction zone so as to remove oxygen and sulfur dioxide from the system prior to introduction of the regenerated sorbent into the sorbent activation zone. The stripping comprises a set of conditions that includes total pressure, temperature and stripping agent partial pressure.

Preferably the total pressure in a stripper, when employed, is in a range of from about 25 psia to about 500 psia.

The temperature for such strippers can be in the range of from about 100° F. to about 1000° F.

The stripping agent is a composition that helps to remove hydrocarbons from the sulfurized solid sorbent. Presently, the preferred stripping agent is nitrogen.

The sorbent regeneration zone employs a set of conditions such that at least a portion of the sulfurized sorbent is desulfurized.

The total pressure in the regeneration zone is generally in the range of from about 10 to about 1500 psia. Presently preferred is a total pressure in the range of from about 25 psia to about 500 psia.

The sulfur removing agent partial pressure is generally in the range of from about 1 percent to about 25 percent of the total pressure.

The sulfur removing agent is a composition that helps to generate gaseous sulfur oxygen-containing compounds such

a sulfur dioxide, as well as to burn off any remaining hydrocarbon deposits that might be present. Currently, oxygen-containing gases such as air are the preferred sulfur removing agent.

The temperature in the regeneration zone is generally from about 100° F. to about 1500° F. with a temperature in the range of about 800° F. to about 1200° F. being presently preferred.

The regeneration zone can be any vessel wherein the desulfurizing or regeneration of the sulfurized sorbent can take place.

The desulfurized sorbent is then reduced in an activation zone with a reducing agent so that at least a portion of the cobalt content of the sorbent composition is reduced to produce a solid cobalt reduced metal sorbent having an amount of reduced metal therein to permit the removal of sulfur components from a stream of cracked-gasoline or diesel fuel.

In general, when practicing the process of this invention, the reduction of the desulfurized solid cobalt-containing sorbent is carried out at a temperature in the range of about 100° F. to about 1500° F. and a pressure in the range of about 15 to 1500 psia. Such reduction is carried out for a time sufficient to achieve the desired level of cobalt reduction in the sorbent system. Such reduction can generally be achieved in a period of from about 0.01 to about 20 hours.

Following the activation of the regenerated particulate sorbent, at least a portion of the resulting activated (reduced) sorbent can be returned to the desulfurization unit.

When carrying out the process of the present invention in a fixed bed system, the steps of desulfurization, regeneration, stripping, and activation are accomplished in a single zone or vessel.

The desulfurized cracked-gasoline resulting from the practice of the present invention can be used in the formulation of gasoline blends to provide gasoline products suitable for commercial consumption.

The desulfurized diesel fuels resulting from the practice of the present invention can likewise be used for commercial consumption where a low sulfur-containing fuel is desired.

## EXAMPLES

The following examples are intended to be illustrative of the present invention and to teach one of ordinary skill in the art to make and use the invention. These examples are not intended to limit the invention in any way.

### Example I

A solid reduced cobalt metal sorbent was produced by dry mixing 20.02 pounds of diatomite silica and 25.03 zinc oxide in a mix Muller for 15 minutes to produce a first mixture. While still mixing, a solution containing 6.38 pounds of Disperal alumina (Condea), 22.5 pounds of deionized water and 316 grams of glacial acetic acid were added to the mix Muller to produce a second mixture. After adding these components, mixing continued for an additional 30 minutes. This second mixture was then dried at 300° F. for 16 hours and then calcined at 1175° F. for one hour to form a third mixture. This third mixture was then particularized by granulation using a Stokes Pennwalt granulator fitted with a 50 mesh screen. 200 grams of the resulting granulated mix was then impregnated with 148 grams of cobalt nitrate hexahydrate dissolved in 43 grams of hot (200° F.) deionized water to produce a particulate impregnated mix. The impregnated particulate was dried at 300° F. for one hour and then calcined at 1175° F. for one hour. 100 grams of the calcined

particulate was impregnated with a solution of 74 grams of cobalt nitrate hexahydrate dissolved in 8 grams of hot deionized water to produce an impregnated particulate product which was then dried at 300° F. for one hour and then calcined at 1175° F. for one hour to form a solid cobalt oxide sorbent.

The solid cobalt oxide sorbent was then reduced by subjecting it to a temperature of 700° F., a total pressure of 15 psia and a hydrogen partial pressure of 15 psi for 30 minutes to produce a solid reduced cobalt sorbent wherein the cobalt component of the sorbent composition was substantially reduced to a zero valence state.

### Example II

The solid reduced cobalt sorbent as prepared in Example I was tested for its desulfurization ability as follows.

A one inch quartz reactor tube was loaded with the indicated amounts of the sorbent of Example I. This solid reduced cobalt sorbent was placed on a frit in the middle of the reactor. Gaseous cracked-gasoline having about 345 parts per million sulfur by weight of the sulfur-containing compounds based on the weight of the gaseous cracked-gasoline and having about 95 weight percent thiophenic compounds (such as for example, alkyl benzothiophenes, alkyl thiophenes, benzothiophene and thiophene) based on the weight of sulfur-containing compounds in the gaseous cracked-gasoline was pumped upwardly through the reactor. The rate was 13.4 milliliters per hour. This produced sulfurized solid sorbent and desulfurized gaseous cracked-gasoline.

In Run 1, hydrogen was added to the gasoline feed at a partial pressure of 6.6 psi (out of a total pressure of 15 psi) resulting in a reduction in gasoline sulfur to 15–25 parts per million.

After Run 1, the sulfurized sorbent was subjected to regeneration conditions that included a temperature of 900° F., a total pressure of 15 psia and an oxygen partial pressure of 0.6 to 3.1 psi for a period of 1–2 hours. Such conditions are hereinafter referred to as “regeneration conditions” to produce a desulfurized cobalt-containing sorbent. This sorbent was then subjected to reducing conditions that included a temperature of 700° F., a total pressure of 15 psia and a hydrogen partial pressure of 15 psi for a time period of 0.5 hours. Such conditions are hereinafter referred to as “reducing conditions”.

In the next series of runs (2–6), after each run the sulfurized sorbent was subjected to regeneration and reducing conditions as described above.

Runs 2 and 3 were essentially repeats of Run 1 indicating that the sorbent can be regenerated to a fresh state where it can reduce the sulfur content of cracked-gasoline to about 5 parts per million.

A composite of product gasoline from each of the Runs 1 and 2 was subjected to a test to determine its research octane number (RON), using a method as described in ASTM 2699 procedure entitled “Research Octane Number of Sparked Ignition Engine Fuel”. The RON for the products from Runs 1 and 2 was 91.4 as compared to the RON of 91.1 for the cracked-gasoline feed, indicating that the octane of the cracked-gasoline was not affected by carrying out the inventive desulfurization process.

In Runs 4–7, the effect of hydrogen partial pressure was studied. As the hydrogen partial pressure is reduced (Run 4), the ability of the sorbent to desulfurize cracked-gasoline diminished. When no hydrogen is used in the process (Run

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5), very little reduction in the sulfur content is effected. When the hydrogen partial pressure was increased to 13.2, the sorbent essentially reduced the cracked-gasoline to less than 5 parts per million.

Run 7 was a repeat of Runs 1–3 and indicates that even after repeated cycles of desulfurization, regeneration and reduction or activation, the ability of the sorbent to remove sulfur from cracked gasoline did not diminish, for example compare Run 1 to Run 7.

The results of this series of runs is set forth in Table 1.

TABLE 1

Reactor	Run Number						
Conditions	1	2	3	4	5	6	7
Amount (grams)	10	10	10	10	10	10	10
TP <sup>1</sup>	15	15	15	15	15	15	15
HPP <sup>2</sup>	6.6	6.6	6.6	2.25	0	13.2	6.6
° F.	700	700	700	700	700	700	700
IOS <sup>3</sup>	Sulfur <sup>4</sup>						
1	15	5	5	75	285	5	15
2	20	5	<5	105	385	<5	15
3	25	5	<5	110	320	<5	10
4	25		5	115		<5	5
5	24		10			<5	10
RON	91.4	91.4					

<sup>1</sup>Total pressure in psia.

<sup>2</sup>Hydrogen particle pressure in psia.

<sup>3</sup>The time on stream in hours.

<sup>4</sup>The amount of sulfur-containing compounds left in the desulfurized cracked-gasoline in parts per million sulfur by weight based on the weight of the desulfurized cracked-gasoline.

The specific examples herein disclosed are to be considered as being primarily illustrative. Various changes beyond those described will no doubt occur to those skilled in the art; and such changes are to be understood as forming a part of this invention insofar as they fall within the spirit and scope of the appended claims.

That which is claimed is:

1. A process for the production of a sorbent composition suitable for the removal of sulfur from a cracked-gasoline or diesel fuel stream which comprises:

- admixing of zinc oxide, silica and alumina so as to form a mix thereof;
- particulating the resulting mix so as to form particles thereof;
- drying the particulate of step (b);
- calcining the dried particulate of step (c);
- impregnating the resulting calcined particulate of step (d) with cobalt or a cobalt-containing compound;
- drying the impregnated particulate of step (e);
- calcining the dried particulate of step (f); and thereafter
- reducing the resulting calcined particulate of step (g) with a suitable reducing agent under suitable conditions to produce a particulate composition wherein the

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valence of essentially all of the cobalt therein is zero such that the reduced cobalt-containing composition will affect the removal of sulfur from a stream of cracked-gasoline or diesel fuel when said stream is contacted with said reduced cobalt-containing composition.

2. A process in accordance with claim 1 wherein said mix is in the form of one of a wet mix, dough, paste or slurry.

3. A process in accordance with claim 1 wherein said particles are in the form of one of granules, extrudates, tablets, spheres, pellets or microspheres.

4. A process in accordance with claim 1 wherein said zinc oxide is present in an amount in the range of from about 10 to about 90 weight percent, said silica is present in an amount in the range of about 5 to about 85 weight percent and said alumina is present in an amount in the range of from 5 about 5 to about 30 weight percent.

5. A process in accordance with claim 4 wherein said particulate is impregnated with cobalt or a cobalt compound in an amount to provide a cobalt content therein in an amount in the range of from about 5 to about 50 weight percent.

6. A process in accordance with claim 1 wherein said particulate is dried in steps (c) and (f) at a temperature in the range of about 150° F. to about 350° F.

7. A process in accordance with claim 1 wherein said dried particulate is calcined in steps (d) and (g) at a temperature in the range of about 400° F. to about 1500° F.

8. A process in accordance with claim 2 wherein said zinc oxide is present in an amount in the range of about 45 to 60 weight percent, said silica is present in an amount in the range of about 15 to 60 weight percent, said alumina is present in an amount in the range of about 5.0 to about 15 weight percent and said cobalt is present in an amount in the range of about 15 to about 40 weight percent.

9. A process in accordance with claim 1 wherein said calcined, impregnated particulated mix is reduced in a reduction zone with a reducing agent under suitable conditions to effect a substantial reduction of the valence of the cobalt content so as to provide an amount of reduced valence cobalt metal such that the resulting composition will effect the removal of sulfur from a cracked-gasoline or diesel fuel when treated with same under desulfurization conditions.

10. A process in accordance with claim 9 wherein said reduced valence cobalt is present in an amount in the range of about 5 to about 40 weight percent, based on the total weight of the sorbent composition.

11. A process in accordance with claim 9 wherein the reduction of cobalt is carried out at a temperature in the range of about 100° F. to about 1500° F. and at a pressure in the range of about 15 to about 1500 psia for a time sufficient to permit the formation of the desired reduced valence cobalt component.

\* \* \* \* \*



# United States Patent [19]

Eberly, Jr. et al.

[11] Patent Number: 4,464,252

[45] Date of Patent: Aug. 7, 1984

[54] ADSORBENTS FOR SULFUR REMOVAL

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[21] Appl. No.: 410,250

[22] Filed: Aug. 23, 1982

[51] Int. Cl.<sup>3</sup> ..... C10G 29/04

[52] U.S. Cl. .... 208/243; 208/244; 208/249; 208/251 R; 502/34; 502/38

[58] Field of Search ..... 208/243, 249, 251 R; 252/411 S; 423/244; 502/38

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[57] ABSTRACT

A process wherein a regenerated, spent sulfided vanadium-containing Group VIII metal, Group VI-B metal, or Group VI-B/Group VIII metals containing catalyst is contacted with a stream of an oxygen-containing gas and the coke burned therefrom to regenerate the catalyst. The regenerated catalyst as such, or after reduction of the catalytic metals by contact with hydrogen, can be used as an adsorbent to remove essentially all of the sulfur from a naphtha feed which contains as much as 50 weight ppm sulfur, and greater.

6 Claims, No Drawings

## ADSORBENTS FOR SULFUR REMOVAL

### FIELD OF THE INVENTION

This invention relates to a process for the desulfurization of hydrocarbon feedstocks, particularly the desulfurization of naphtha feeds with vanadium and nickel or cobalt containing adsorbents.

### BACKGROUND OF THE INVENTION AND PRIOR ART

The use of catalysts formed by supporting Group VIII non-noble metals and Group VI-B metals (Periodic Table of the Elements, E. H. Sargent & Company; Copyright 1962 Dyna-Slide Co.), e.g., Ni/Mo, Co/Mo, Ni/Co/Mo, Ni/W, Co/W, Ni/Co/W and the like upon porous refractory inorganic oxides, particularly alumina, to catalytically remove sulfur from petroleum fractions, crude oils, and other mixtures of hydrocarbons has been known for many years. Sulfur removal is necessary since its presence in appreciable amounts gives rise to serious corrosion and refining problems. In many refinery processes, especially those using catalysts, feed sulfur is very deleterious in that it causes excessive catalyst deactivation and loss of yield of the desired product. Gasoline should be relatively free of sulfur to make it compatible with lead anti-knock compounds, and to improve its color and odor stability. In particular, in reforming (hydroforming) processes used to make high octane gasoline, sulfur compounds, even in the 1-20 parts per million, (wppm) range contribute to loss of catalyst activity and C<sub>5</sub><sup>+</sup> liquid yield. In the last decade, in particular, polymetallic metal catalysts have been employed to provide, at reforming conditions, improved catalyst activity, selectivity and stability. Thus, additional metallic components have been added to the more conventional platinum catalysts as promoters to further improve, particularly, the activity or selectivity, or both, of the basic platinum catalyst, e.g., iridium, rhenium, selenium, tin, and the like. In the use of these catalysts it has become essential to reduce the feed sulfur to only a few wppm. For example, in the use of platinum-rhenium catalysts it is generally necessary to reduce the sulfur concentration of the feed well below about 2 wppm, and preferably well below about 0.1 wppm, to avoid excessive loss of catalyst activity and C<sub>5</sub><sup>+</sup> liquid yield. By removing virtually the last traces of sulfur from the naphtha feed, considerable improvement in activity and C<sub>5</sub><sup>+</sup> liquid yield of high octane product are achieved. Stability advantages also occur enabling longer catalyst life and run length to be realized.

The sulfur-containing feed, prior to reforming, is generally treated over a hydrofining catalyst, e.g., a Co/Mo catalyst, and major amounts of the sulfur are catalytically removed in the form of hydrogen sulfide, H<sub>2</sub>S. However, due to the presence of small amounts of olefins, it is possible for some of the H<sub>2</sub>S to recombine with the olefins upon cooling and to form trace amounts of undesirable sulfur compounds predominantly in the form of mercaptans. This trace residual sulfur can then be removed from the naphtha reformer feed by adsorption over copper chromite or catalysts containing nickel. These metals have been found useful per se, or have been supported on high surface area refractory inorganic oxide materials such as alumina, silica, silica/alumina, clays, kieselguhr, and the like. For example, a massive nickel catalyst containing 50-60%

nickel on kieselguhr has been used. Such catalysts become sulfur saturated, and in the present state-of-the-art are not generally regenerated, but discarded or processed for metals recovery.

The earlier mentioned Group VI-B/VIII catalysts have thus conventionally been used to hydroprocess, or hydrosulfurize, various hydrocarbon fractions to catalytically remove not only sulfur, but also nitrogen, from the hydrocarbon fractions. In hydroprocessing such feeds as vacuum gas oils, atmospheric or vacuum residua, shale, coal liquid fractions and the like, however, not only is sulfur removed from the feed, but also nickel and vanadium. As a result, these metals together with sulfur, carbonaceous material, or coke, and other materials are deposited on the catalysts gradually rendering them inactive. Thus, the catalyst not only contains its original metals, but additionally nickel and vanadium. After extended use, the catalyst becomes sufficiently inactive that it is no longer suitable for use in commercial operation, and hence it must be replaced. It has little value, and in conventional practice it is replaced by a fresh catalyst.

### THE INVENTION

In accordance with the present invention, a spent Group VI-B and/or Group VIII metal containing catalyst having had deposited on it, by virtue of its use, coke, sulfur and/or additional nickel and vanadium is regenerated by contact with a stream of an oxygen-containing gas, preferably air, or air/inert mixture, or oxygen-enriched air and the coke burned therefrom, such regeneration converting the metals to their oxides, and perhaps to some extent to their sulfates. The regenerated catalyst as such, or after reduction of the catalytic metals by contact with hydrogen, can be used as an adsorbent to remove essentially all of the sulfur from a naphtha feed which contains as much as 50 wppm sulfur or greater.

A bed of the regenerated vanadium-containing Group VI-B, Group VIII, or Groups VI-B/VIII metals catalyst is contacted with a naphtha feed containing generally from about 1 wppm to about 50 wppm, preferably from about 1 wppm to about 10 wppm sulfur. The feed is passed therethrough to remove sufficient of the sulfur-containing compounds from the feed to provide a sulfur level in the product of 0.2 wppm, or less; and preferably, 0.1 wppm, or less. Suitably, the bed of spent catalyst is contacted with the naphtha at temperatures ranging from about 100° F. to about 600° F., preferably from about 300° F. to about 500° F., at pressures ranging from about atmospheric to about 600 psig, preferably from about 100 psig to about 400 psig, and at space velocities ranging from about 0.1 V/V/Hr to about 30 V/V/Hr, preferably from about 1 V/V/Hr to about 20 V/V/Hr. The desulfurization of the naphtha feed is accomplished either in the absence or presence of added hydrogen. Preferably, hydrogen is not used. However, some hydrogen can be employed sufficient to saturate the hydrocarbon liquid at the temperature and pressure of the adsorption unit. Or it can be added to the extent of 1 to 200 SCF/B. Contact of the sulfur-containing feed with the bed of catalyst is continued to the point of breakthrough of sulfur in the exit effluent from the bed. In the preferred case, breakthrough is characterized by a sulfur content in the exit stream significantly exceeding 0.1 wppm S.

The invention, and its principle of operation, will be more fully understood by reference to the following examples and comparative data.

### EXAMPLE

Two catalysts, designated Catalysts A and B, were obtained from catalyst manufacturers. Catalyst A is a nickel-containing material consisting of 73% Ni expressed as the oxide admixed or impregnated upon kieselguhr, otherwise known as diatomaceous earth, a naturally occurring form of silica. Catalyst B, is a standard Ni/Mo catalyst used for the catalytic desulfurization of petroleum and other hydrocarbonaceous streams. Catalyst C, is a spent hydrosulfurization catalyst originally consisting of Ni and Mo supported on alumina. Prior to regeneration, this catalyst contained 13.41% carbon and 5.95% sulfur by weight. The catalyst was regenerated by contacting with an oxygen/nitrogen mixture and burning off the coke and sulfur at 600° F.-800° F. over a period of 24 hours. After regeneration, the carbon and sulfur contents were 0.1% and 2.13%, respectively. An analysis of each catalyst is given in Table I.

TABLE I

% by Weight	Catalyst A	Catalyst B	Catalyst C
NiO	73	5.5	6.3
SiO <sub>2</sub>	27	—	0.0
Al <sub>2</sub> O <sub>3</sub>	0	81.9	77.1
MoO <sub>3</sub>	0	12.6	10.4
V <sub>2</sub> O <sub>5</sub>	0	0	6.3

To test these catalysts, each was reduced at 700° F. with atmospheric hydrogen, and then a 5 gram portion thereof was placed in an autoclave. An amount of 580 ml of a naphtha containing 2500 wppm S as n-hexylmercaptan was then added. The autoclave was then pressurized with hydrogen to 275 psig and heated to 350° F. with vigorous stirring. After contacting each catalyst for 16 hours, a sample of liquid was withdrawn and analyzed for sulfur content. From the reduction in sulfur content, the amount of sulfur retention on the catalyst was determined. Results using Catalysts A, B, and C are listed in Table II.

TABLE II

AUTOCLAVE EXPERIMENT			
Charge:	580 ml of Arabian Naphtha Spiked with n-Hexyl Mercaptan to Contain 2500 wppm S		
Catalyst:	5 Grams of 60-80 Mesh Particles		
Conditions:	350° F., 275 psig, 16 hr Contact Time		
Catalyst	Wt. % S	S/Ni Atomic Ratio	
A	22.5	0.928	
B	6.5	2.95	
C	10.9	4.53	

These data show that Catalyst A adsorbs the most sulfur. This is not completely unexpected since the material contains 73% Ni as expressed in the form of NiO.

The sulfur uptake corresponds to 0.928 atoms S/atom Ni. The Ni/Mo catalyst, on the other hand, is able to adsorb 6.5% sulfur by weight, corresponding to 2.95 atoms S/atom Ni. However, it is quite possible that the molybdenum is also capable of combining, and hence may in fact combine with the sulfur compound. In any event however, the significance underlying this invention is best seen by the performance of catalyst C. This material adsorbs 10.9% sulfur, which corresponds to 4.53 atoms S/atoms Ni, although here again the Mo as well as the V compounds may be absorbing sulfur, it is quite clear that the presence of the vanadium enhances sulfur adsorption.

Thus, vanadium addition is beneficial for improving the sulfur retention of the Ni/Mo catalyst. Such a catalyst is very cheaply obtained as a discharged hydrofining catalyst or catalyst used for residual conversions.

It is apparent that various modifications and changes can be made without departing the spirit and scope of the invention.

Having described the invention, what is claimed is:

1. A process for the removal of sulfur from a sulfur-containing hydrocarbon feed which comprises contacting said sulfur-containing hydrocarbon feed with a bed of spent regenerated hydrofining catalyst consisting essentially of vanadium and a Group VIII metal, or a Group VI-B metal, or both Group VI-B/Group VIII metals deposited on a support, said support comprising alumina.

2. The process of claim 1 wherein, prior to contact of the sulfur containing hydrocarbon feed with said bed of catalyst, the catalyst is used in a hydroprocessing reactor wherein coke and metals are deposited, said coked catalyst is then regenerated by contact with a stream of an oxygen-containing gas, and the coke burned therefrom.

3. The process of claim 2 wherein the catalyst, after the coke is burned therefrom, is reduced by contact with hydrogen.

4. The process of claim 1 wherein the regenerated vanadium-containing Group VI-B, Group VIII, or Groups VI-B/VIII metals catalyst is contacted with a naphtha feed containing generally from about 1 wppm to about 50 wppm sulfur.

5. The process of claim 4 wherein the feed contains from about 1 wppm to about 10 wppm sulfur and the feed passed therethrough removes sufficient of the sulfur-containing compounds from the feed to provide a sulfur level in the product of 0.2 wppm, or less.

6. The process of claim 1 wherein the sulfur-containing hydrocarbon feed is a naphtha, and the bed of spent, regenerated catalyst is contacted with the naphtha at temperatures ranging from about 100° F. to about 600° F., at pressures ranging from about atmospheric to about 600 psig, and at space velocities ranging from about 0.1 V/V/Hr to about 30 V/V/Hr.

\* \* \* \* \*

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
21 March 2002 (21.03.2002)

PCT

(10) International Publication Number  
**WO 02/22763 A1**

(51) International Patent Classification<sup>7</sup>: **C10G 29/16**,  
25/00, 25/06, 25/12

(21) International Application Number: PCT/US01/26019

(22) International Filing Date:  
12 September 2001 (12.09.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
60/232,165 11 September 2000 (11.09.2000) US

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(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,  
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,  
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,  
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,  
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,  
MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI,  
SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU,  
ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM,  
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian  
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European  
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,  
IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF,  
CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD,  
TG).

**Published:**

— with international search report

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: PROCESS FOR DESULFURIZING HYDROCARBON FUELS AND FUEL COMPONENTS

(57) Abstract: Processes are disclosed for removing sulfur, including cyclic and polycyclic organic sulfur components such as thiophenes and benzothiophenes, from a hydrocarbon feedstock including fuels and fuel components. The feedstock is contacted with a regenerable sorbent material capable of selectively adsorbing the sulfur compounds present in the hydrocarbon feedstock in the absence of a hydrodesulfurization catalyst. In one embodiment, the sorbent can be an active metal oxide sulfur sorbent in combination with a refractory inorganic oxide cracking catalyst support. In another embodiment, the sorbent can be a metal-substituted refractory inorganic oxide cracking catalyst wherein the metal is a metal which is capable in its oxide form, of adsorption of reduced sulfur compounds by conversion of the metal oxide to a metal sulfide. The processes are preferably carried out in a transport bed reactor.

## **PROCESS FOR DESULFURIZING HYDROCARBON FUELS AND FUEL COMPONENTS**

### **FIELD OF THE INVENTION**

The present invention relates to the desulfurization of hydrocarbons, particularly hydrocarbon fuels and hydrocarbon fuel components and their precursors. More particularly, the present invention relates to removal of sulfur, primarily organic sulfur, contaminants including organic sulfides, disulfides, mercaptans, thiophenes, benzothiophenes, and dibenzothiophenes, from hydrocarbon fuels such as gasoline, diesel fuels, aviation fuels, and from components and precursors of such fuels such as FCC naphtha, i.e., naphtha from a fluid catalytic cracker (FCC), FCC light cycle oil, coker distillate, and the like.

### **BACKGROUND OF THE INVENTION**

Currently available gasoline contains sulfur contaminants at an average cumulative level exceeding 300 parts per million by weight (ppmw) of sulfur (i.e., calculated based on sulfur weight). On-road application diesel fuel has a higher sulfur content ranging typically from 300 to 2,000 ppmw. Combustion of gasoline and diesel fuels during use in internal combustion engines, in turn, converts the sulfur contaminants into sulfur oxides. The sulfur oxides are environmentally undesirable and also have been found to have a long-term deactivation impact on automotive catalytic converters that are used to remove nitrogen oxide and unburned hydrocarbon contaminants from automotive emissions.

In order to improve air quality, environmental protection agencies of various industrialized countries have therefore announced or proposed new regulations requiring reduction in sulfur content of gasoline, diesel, and other motor fuels. In the United States, the Environmental Protection Agency (EPA) is requiring that the sulfur content of gasolines be reduced to a maximum of 30 ppmw by the year 2005 under recently implemented Tier 2 regulations. Similarly, the EPA has enacted regulations to bring down the sulfur levels in diesel fuel used for on-road application to 15 ppmv

or below by 2006. It is anticipated that due to public demand for a cleaner environment, the future will bring calls for even stricter sulfur oxide emissions and fuel specifications; and, as a result, fuels containing nearly zero sulfur levels are being discussed. Accordingly, the new regulations will require sulfur reduction of typically 90% or more by 2005, and perhaps complete sulfur removal thereafter. At the same time, the sulfur content of commercially available crude oils produced in the United States and in neighboring American countries has been generally increasing; thus the new regulations will require more drastic sulfur reduction in the future. Further reductions meeting nearly zero sulfur levels required by expected future regulations will exacerbate this problem further.

Various technologies are currently available or have been proposed which are believed to be capable of reducing sulfur contaminants in gasoline to 30 ppmw or less. According to a recent study conducted by EPA, these available and proposed technologies include hydrotreating and adsorption-based processes (see Regulatory Impact Analysis--Control of Air Pollution From New Motor Vehicles: Tier 2 Motor Vehicle Emissions Standards and Gasoline Sulfur Control Requirements, EPA 420-R-99-023, United States Environmental Protection Agency, December 1999, Chapter IV, pp. IV-42--IV-65).

As detailed in the EPA study, the sulfur content of current gasolines is attributable primarily to fluidized catalytic crackers (FCC), or to coker units, which convert heavy boiling stocks to gasoline components or precursors, i.e., naphthas. It has been reported that more than 90% of the sulfur in gasoline comes from streams produced in the FCC unit. The sulfur content of FCC naphtha varies from 150 to 3,000 ppmw depending upon the sulfur concentration of feed and the endpoint of the gasoline product. Accordingly, reduction of sulfur in motor gasoline can be accomplished by FCC feed hydrotreating or by hydrotreating the naphtha cut obtained from the FCC unit. The latter process is preferred because of substantially lower cost resulting from substantially lower volumes of the feedstocks to be processed.

Nevertheless, hydrotreating of FCC naphtha is expensive, both in capital investment, and in operating costs. In particular, hydrotreating of FCC naphtha is typically carried out in a packed-bed or a fixed-bed reactor using various well-known hydrodesulfurization (HDS) catalysts. These catalysts typically contain a Group 8

(other than iron), 9, or 10 transition metal such as cobalt and/or nickel combined with a Group 6 transition metal, particularly molybdenum or tungsten, on a high surface area alumina support ("Group metal" as used herein is based on the new IUPAC format for the Periodic Table of the Elements, which numbers the groups from 1 to 18 in Arabic numerals). Before their use, these catalysts are typically pre-sulfided under controlled reducing conditions to impart their HDS catalytic activity. Other HDS catalysts include platinum, palladium, or like metals supported on alumina. In the presence of HDS catalysts, organic sulfur compounds present in FCC naphtha react with hydrogen and are converted into hydrogen sulfide at temperature and pressures or 300 to 500°C, and 400 to 600 psig. The hydrogen sulfide thus formed can be subsequently and readily removed in a downstream unit by sorbents or other processes such as a combination of amine and Claus processes.

However, during the HDS hydrotreating process, octane number loss can occur by saturation of high-octane containing olefins that are present in FCC naphtha. Moreover, increased olefin saturation is accompanied by increased hydrogen consumption and cost. In addition, there can be a loss in gasoline yield caused by mild cracking which breaks some of the naphtha into smaller, lighter fractions, which are too light for blending into gasoline.

Three proven hydrotreating desulfurization technologies are identified in the EPA report cited previously. However, octane number loss remains a serious problem with all three proven technologies particularly when applied for removal of 90 percent or more sulfur from the FCC naphtha to meet EPA's Tier 2 requirements.

Newly proposed technologies identified in the EPA report include a catalytic distillation technology, called CDTech, which relies upon an HDS catalyst supported in a distillation column to provide reaction of organic sulfur compounds with diene compounds present in FCC naphtha. The resultant thioether reaction product has a higher boiling point and can be removed from the bottom of the distillation column. Similar to conventional hydrotreating processes, this process also uses an HDS catalyst. However, hydrogen consumption and olefin saturation are claimed to be lower compared to conventional hydrotreating processes. The operating cost for sulfur removal using the CDTech process is reported to be 25% lower than conventional hydrotreating processes for the same degree of sulfur removal.

Two emerging adsorption-based desulfurization processes are also discussed in the EPA report. One process, named IRVAD, adsorbs heteroatom-containing hydrocarbon compounds, including sulfur, nitrogen, and oxygen compounds, present in FCC naphtha onto an alumina-based adsorbent in liquid phase (see U.S. Patent 5,730,860, issued March 24, 1998 to Irvine). The adsorbent is fluidized in a tall column and continuously removed and regenerated using hydrogen in a second column. The regenerated catalyst is then recycled back into the reactor. The regeneration of spent adsorbent produces a hydrocarbon stream containing about 1 wt% sulfur, which can be treated using conventional processes. While the inventors have claimed an overall cost of sulfur removal as low as 0.77 cents per gallon of gasoline compared to 5 to 8 cents for conventional hydrotreating processes, serious process and system integration issues still remain with this technology, which are hampering its commercial deployment.

The other emerging adsorption-based desulfurization technology named as the SZorb process is being developed by the Phillips Petroleum Company. It is understood that this process uses an adsorbent/catalyst comprising one or more metallic promoters, such as a combination of nickel and cobalt, in a zero valence state to selectively remove sulfur compounds from FCC naphtha in the presence of hydrogen. As the adsorbent/catalyst becomes saturated with sulfur compounds, it is sent to a regeneration unit where it is treated with an oxygen-containing gas for removal of the sulfur as sulfur dioxide. The oxidized adsorbent/catalyst is further treated with hydrogen in a downstream reducing unit presumably to reduce some of the metal oxide/s present in the adsorbent/catalyst composition to their reduced forms. The reduced adsorbent/catalyst is then fed to the sulfur removal unit, along with hydrogen, for further desulfurization of FCC naphtha. This process is carried out at a temperature between about 250 to about 350°C (about 500 to about 700°F) and a pressure of 100 to 300 psig. Phillips proposes to use conventional bubbling-bed fluidized-beds for adsorption and regeneration reactors, which will have inherent limitation on throughput of the FCC naphtha feed that can be processed in this system. Phillips claims that this process can remove about 97% of the sulfur from FCC naphtha with a 1 to 1.5 point loss in octane number and with an operating cost of 1.5 to 2 cents per gallon of gasoline. However, the need for a two-step regeneration



process, consumption of hydrogen and associated octane number loss, and the use of low throughput bubbling-bed systems are some of the major drawbacks of this technology. Recent information from Phillips indicates that this process is being adapted for desulfurization of diesel.

Various other desulfurization processes are known or have been proposed. For example, U.S. Patent 3,063,936, issued on November 13, 1962 to Pearce et al. discloses that sulfur reduction can be achieved for straight-run naphtha feedstocks from 357 ppmw to 10-26 ppmw levels by hydrotreating at 380°C using an alumina-supported cobalt molybdate catalyst. According to Pearce et al., a similar degree of desulfurization may be achieved by passing the straight-run naphtha with or without hydrogen, over a contact material comprising zinc oxide, manganese oxide, or iron oxide at 350 to 450°C. Pearce et al. propose to increase sulfur removal by treating the straight run naphtha feeds in a three-stage process in which the hydrocarbon oil is treated with sulfuric acid in the first step, a hydrotreating process employing an alumina-supported cobalt molybdate catalyst is used in the second step, and an adsorption process, preferably using zinc oxide is used for removal of hydrogen sulfide formed in the hydrotreating step as the third step. The process is said to be suitable only for treating feedstocks that are substantially free from ethylenically or acetylenically unsaturated compounds. In particular, Pearce et al. disclose that the process is not suitable for treating feedstocks, such as hydrocarbons obtained as a result of thermal cracking processes that contain substantial amounts of ethylenically or acetylenically unsaturated compounds such as full-range FCC naphtha, which contains about 30% olefins.

U.S. Patent 5,157,201 discloses that organic sulfur species, primarily comprising organic sulfides, disulfides, and mercaptans, can be adsorbed from olefin streams, without saturating the olefins, by contacting the feed with a metal oxide adsorbent at relatively low temperatures (50 to 75°C), in the absence of hydrogen. The metal oxide adsorbent includes metal oxides selected from a group consisting of a mixture of cobalt and molybdenum oxides, a mixture of nickel and molybdenum oxides and nickel oxide supported on an inert support. The adsorbed organic sulfur compounds are removed from the sorbent by purging with an inert gas while heating at a temperature of about 200°C for at least about 45 minutes. Although such low-

temperature adsorption processes avoid any olefin saturation, these processes are limited to removal of lighter sulfur compounds such as mercaptans and organic sulfides and disulfides. These processes cannot be used effectively for removal of thiophenes, benzothiophenes, and higher cyclic sulfur compounds, which typically account for greater than 50% of the sulfur in FCC naphtha.

In summary, currently available and proposed technologies for reducing sulfur content of FCC naphtha feedstocks to levels of 30 ppmw or less are capital intensive, operationally complex, typically require significant hydrogen consumption, can severely reduce octane number values and/or result in loss in yield, and rely on expensive hydrotreating catalysts in whole or in part. In addition, the existing and proposed technologies rely on fixed-bed or bubbling-bed reactors resulting in limited throughputs and substantial capital investment.

#### SUMMARY OF THE INVENTION

The present invention accomplishes sulfur reduction in gasoline and diesel fuels, components and precursors of gasoline and diesel fuels such as naphthas, i.e., full and medium range FCC naphthas, coker naphthas, straight run naphthas, visbreaker naphthas, and thermally cracked naphthas, light cycle oils, coker distillates, straight-run diesel, hydrocracker diesel, and the like, without relying on hydrotreating processes that employ costly transition metal HDS catalysts. Accordingly, the invention can minimize or eliminate various known disadvantages of conventional and proposed desulfurization processes for producing low-sulfur gasoline and diesel fuels, including octane number loss, olefin content reduction, and/or yield loss in desulfurized products, hydrogen consumption and its associated costs, the high cost of manufacturing and regenerating HDS catalysts, and the disposal costs associated with various environmentally undesirable HDS catalysts. In preferred embodiments, the present invention can accomplish substantial sulfur removal at high throughput levels, thereby allowing a significant reduction in the capital investment required to achieve large scale production of low-sulfur gasoline, diesel, and related fuels.

In accordance with one aspect of the present invention, a normally liquid hydrocarbon fuel or fuel component, such as an FCC naphtha, FCC light cycle oil, coker distillate, straight run diesel fraction, or the like, is treated at an elevated

temperature, preferably a temperature above about 300°C (572°F), with an active metal oxide sulfur sorbent, preferably a zinc oxide-based or iron oxide-based sorbent, in the absence of an active HDS catalyst, to reduce sulfur contaminant levels to less than about 30 ppmw, sulfur. Sulfur-laden sorbent is separated from the desulfurized hydrocarbon product and is preferably regenerated by treatment with an oxygen-containing gas, e.g., air, and then recycled for use in the desulfurization operation. The invention is applicable to hydrocarbon fuels and to hydrocarbon fuel fractions and precursors, of various sulfur contents, for example: FCC naphtha having an average sulfur content of between about 150 and about 3,000 ppmw, more typically, between about 500 to about 2,000 ppmw; diesel fuel blends, precursors and fractions such as light cycle oil, coker distillate and straight run diesel fractions having an average sulfur content between about 5,000 and about 30,000 ppmw, more typically, between about 7,000 and about 20,000 ppmw. The process of this invention is equally applicable to partially desulfurized feedstocks such as hydrotreated FCC naphtha and diesel, to reduce their sulfur content to below 30 ppmw.

The process of the invention can be carried out with or without addition of hydrogen to the feed; however, it is preferred to add a sufficient amount of hydrogen to the feed to avoid coking of the feed as it is heated to the elevated temperatures required for desulfurization. Because no active HDS catalyst is used in the present process, hydrogen addition to minimize coking can typically be achieved with minimal or substantially no hydrogen consumption so that the hydrogen can be recovered from the desulfurized process effluent and recycled. Moreover, because of the substantial absence of an HDS catalyst, saturation of desirable olefins in the hydrocarbon feed can be avoided or minimized even at high temperature reaction conditions, and even in the presence of added hydrogen. Furthermore, the hydrogen gas stream used in the process can be of relatively low purity; for example, a waste stream containing hydrogen, as may be found in a refinery or petrochemical plant. Moreover, because no active HDS catalyst is required in the present invention, no hydrogen treatment is required for regeneration or reactivation of the sorbent.

The present inventors have further found that the active metal oxide sulfur sorbents, particularly zinc oxide-based and iron oxide-based sorbents, when used in combination with a refractory inorganic oxide cracking catalyst, e.g., alumina, are

capable of removing both straight chain organic sulfur components such as organic sulfides, disulfides, and mercaptans, and cyclic organic sulfur components including substituted and unsubstituted thiophenes, benzothiophenes, and, to some extent, dibenzothiophenes from hydrocarbon fuels, their fractions and precursors, without hydrotreating. In this regard, the present inventors have discovered that a refractory inorganic oxide cracking catalyst, such as alumina, silica, an aluminosilicate or a metal stabilized refractory inorganic oxide cracking catalyst such as metal stabilized alumina, when used to support, or otherwise in combination with the active metal oxide sulfur sorbent, has catalytic activity for selectively cracking cyclic organic sulfur compounds to provide a hydrocarbon and a sulfur species. The sulfur species can be captured by the cracking catalyst or by the active metal oxide sulfur sorbent as a metal sulfide or a metal-sulfur complex. Although prior art processes have primarily relied on hydrotreating of FCC naphthas and diesel fuel fractions and components using HDS catalysts to convert organic sulfur contaminants to hydrogen sulfide, followed by amine and Claus process treatments for removal of hydrogen sulfide, it has now been found that active metal oxide sorbents, preferably zinc oxide-based and iron oxide-based sorbents, supported on or otherwise combined with a refractory inorganic oxide cracking catalyst, can directly remove organic sulfur contaminants from hydrocarbon feedstocks at elevated temperatures without requiring use of an active HDS catalyst. In turn, detrimental aspects of hydrotreating-desulfurization processes, such as octane number reduction, and/or olefins loss, can be minimized or avoided in accord with the present invention.

The active metal oxide sulfur sorbents and refractory inorganic oxide cracking catalyst are preferably used simultaneously to treat the hydrocarbon fuel feed; however they can alternatively be used sequentially in the process of the invention. In preferred embodiments in which the active metal oxide sulfur sorbent and the refractory inorganic oxide cracking catalyst are used simultaneously, the active metal oxide sulfur sorbent is supported on or combined with a refractory inorganic oxide cracking catalyst such as alumina, silica, aluminosilicate, zeolite or the like. This can also provide high temperature stability and extremely high attrition resistance to the sorbent particles.

According to another aspect of the invention, it has been found that certain metal-substituted refractory inorganic oxide cracking catalysts can remove organic sulfur compounds from hydrocarbon feeds, and can also remove sulfur from at least some of the organic sulfur compounds in hydrocarbon feeds, particularly cyclic sulfur compounds such as thiophenes and benzothiophenes, without requiring use of an HDS catalyst or hydrotreating of the feed. The metal, which can be zinc in one currently preferred embodiment, or iron in another currently preferred embodiment, is more generally selected from the group of metals, which are capable in their oxide form, of removing reduced sulfur compounds from gaseous streams by conversion of the metal oxide to a metal sulfide, such metal oxides being known in the art. The refractory inorganic oxide cracking catalyst can be fully, or only partially, reacted with the metal. The metal-substituted refractory inorganic oxide cracking catalyst can be prepared according to processes well known in the art and is advantageously prepared by partially or fully reacting a metal oxide sulfur sorbent with a refractory inorganic oxide cracking catalyst, such as alumina, silica, an aluminosilicate or the like, to form the corresponding metal aluminate, silicate, aluminosilicate or the like. Suitable active metal oxide sorbents for use in the process of the invention include sorbents based on zinc oxide, zinc titanate, zinc ferrite, iron oxide, iron titanate, manganese oxide, cerium oxide, copper oxide, copper cerium oxide, copper ferrite, copper titanate, copper chromium oxide, vanadium oxide, calcium oxide, calcium carbonate, magnesium oxide, magnesium carbonate, and mixtures thereof.

In particular, the metal-substituted inorganic oxide cracking catalyst sorbent, i.e., metal aluminate, silicate, aluminosilicate or the like, can achieve full or partial conversion of organic sulfur compounds, including cyclic sulfur compounds such as thiophenes and benzothiophenes, to a metal sulfide or a metal-sulfur complex. Such metal-substituted inorganic oxide cracking catalyst sorbents can be used in accordance with the invention to treat a hydrocarbon fuel component, precursor, or blend, preferably an FCC naphtha, or a diesel fuel precursor, component, or blend, at an elevated temperature, preferably above about 300°C (572°F), and the treated hydrocarbon stream is then separated from the sulfur-laden sorbent to provide a hydrocarbon product having a sulfur contaminant level preferably of less than about 30 ppmw, without requiring hydrotreating of the feed using an active HDS catalyst.

Moreover, such metal-substituted inorganic oxide cracking catalyst sorbents also possess high mechanical strength and attrition resistance. Currently preferred metal-substituted inorganic oxide materials include zinc aluminate, iron aluminate and combinations thereof.

In preferred embodiments of the invention, the sulfur-laden sorbent employed in the desulfurization process of the invention is regenerable by treatment with oxygen at an elevated temperature. According to one currently preferred embodiment of the invention, the regenerable sorbent is an active metal oxide sulfur sorbent supported on, or otherwise combined with a metal-substituted refractory inorganic oxide cracking catalyst, wherein all or a portion of the metal component of the metal-substituted refractory inorganic oxide is the same metal as the metal of the active metal oxide sulfur sorbent. In particular, such regenerable sorbents are used to remove sulfur compounds from a hydrocarbon fuel component feed, to achieve sulfur contaminant levels of less than about 30 ppmw of total sulfur in the product effluent, without requiring hydrotreating of the feed using an active HDS catalyst. The combination of the metal oxide sulfur sorbent and metal refractory inorganic oxide cracking catalyst, e.g., zinc oxide/zinc aluminate or iron oxide/iron aluminate, can be particularly desirable to prevent or minimize deactivation of the sulfur removal activity of the sorbent during the adsorption-regeneration process. In a currently preferred embodiment, a zinc titanate and/or iron oxide sorbent is supported on an alumina or a metal aluminate, preferably zinc and/or iron aluminate, support.

The sulfur-laden sorbent used to remove sulfur compounds from hydrocarbon feedstocks in the process of the present invention, is regenerated by contacting the sorbent with an oxygen-containing gas, preferably air, at a temperature sufficient to cause the sulfur present on the sorbent to react with oxygen to form sulfur dioxide. Typically, the equilibrium temperature in the regeneration zone will exceed a temperature of about 425°C (800°F). In one preferred embodiment of the invention, regeneration can be initiated or supplemented by addition of the metal sulfide additives disclosed in U.S. Patent 5,914,288, issued on June 22, 1999 to Turk et al.; the disclosure of which is incorporated herein by reference. As disclosed in the aforesaid Turk et al. patent, a preferred metal sulfide initiator is iron pyrite mineral ore.

The regeneration reaction converts the sulfur-laden sorbent, to the active metal oxide form, for example, to zinc or iron oxide, zinc titanate, or zinc or iron aluminate, and the regenerated sorbent is returned directly to the desulfurization zone. Because the sorbents used in the process of the present invention do not include an active HDS catalyst component, no separate hydrogenation treatment is necessary for regenerating the sorbents to an active state. Accordingly, the energy cost, hydrogen consumption, and reaction vessels required for hydrogen treatment of hydrogenation catalysts are avoided in the process of the present invention.

In one preferred embodiment the invention, the desulfurization process is carried out employing a transport bed reactor with a vapor residence time of less than about 20 seconds, more typically less than about 10 seconds. Nevertheless, high sulfur containing hydrocarbon feedstocks, i.e., having a sulfur content greater than about 150-300 ppmw, more typically greater than about 600 ppmw, can be desulfurized in accord with the invention to achieve sulfur reduction to less than 30 ppmw, more typically less than 10 ppmw. The extremely high throughput process according to this aspect of the invention greatly reduces capital investment since a relatively small reactor can be used for treating substantial quantities of hydrocarbon feedstocks. Use of a high throughput transport reactor is possible because of the extremely high attrition resistance of preferred sorbents used in the present invention. This unique combination of extremely high attrition resistance, allowing these sorbents to be used in a transport reactor, and relatively high activity for selectively cracking cyclic sulfur compounds in hydrocarbon feedstocks combined with sorption activity of active metal oxide component of the sorbent for various inorganic and organic sulfur compounds provides significant benefits and advantages as compared to processes of the prior art.

In another preferred embodiment of the invention, the desulfurization process is carried out employing a bubbling bed reactor to treat hydrocarbon fuel feedstocks having an initial sulfur content greater than about 150-300 ppmw, more typically greater than about 600 ppmw, in order to achieve sulfur reduction to less than 30 ppmw, more typically less than 10 ppmw. Bubbling bed reactors, which can provide excellent gas-solid contact and significant process and capital cost benefits as

compared to prior art fixed and packed bed processes, can be employed in accord with the invention using various preferred, high attrition resistance sorbents.

According to another aspect of the invention, sulfur contaminants are removed from an FCC hydrocarbon stream by treating the stream under conventional FCC process conditions, with a regenerable sorbent comprising an active metal oxide sulfur sorbent supported on, or otherwise combined with a refractory inorganic oxide cracking catalyst, preferably comprising a metal substituent, as discussed previously. Advantageously, desulfurization of the FCC hydrocarbon process stream is accomplished simultaneously with the FCC process by adding the sorbent to the FCC riser, e.g., as an additive to the FCC catalyst. According to this aspect of the invention, sulfur compounds initially present in the FCC feedstock, or generated during the FCC process, are selectively captured by the sorbent in the FCC riser. The sulfur-laden sorbent is then sent to the FCC regenerator along with the carbon-laden FCC catalyst where it is regenerated by the oxygen-containing gas, typically air, which is used to regenerate the FCC catalyst. During regeneration, sulfur carried by the sorbent is converted to a sulfur dioxide-containing gas stream that can be treated for sulfur removal in a downstream process unit such as a sulfur dioxide scrubber.

Desulfurization in combination with an FCC operation according to this aspect of the invention is particularly desirable since most of the sulfur (>90%) in gasoline comes from the naphtha produced by conventional FCC treatment. In this regard, the FCC operation is used to upgrade the less desirable portions in crude oil as is well known to those skilled in the art. Because such less desirable portions of oil include substantial quantities of undesirable sulfur-containing components, the product streams generated by the FCC unit also have high sulfur contents. Thus, although some of the sulfur initially in the feed to a conventional FCC unit is removed as  $\text{H}_2\text{S}$  generated during cracking and is collected as non-condensable gas, a substantial portion of the sulfur remains in the FCC product as organic sulfur contaminants, distributed among the various FCC product fractions including FCC naphtha, light cycle oil (LCO), heavy cycle oil (HCO) and the bottoms fraction. Typical sulfur compounds found in FCC naphtha and LCO are essentially heavy thiophenic materials, which are very difficult to convert into  $\text{H}_2\text{S}$  during the catalytic cracking process in a FCC reactor.



According to this aspect of the invention, the active metal oxide sulfur sorbent is added to the FCC catalyst in an amount sufficient to achieve removal of at least about 50 wt.% of sulfur compounds from the FCC naphtha product, i.e., the FCC liquid product fraction having a final boiling point (FBP) less than about 430°F. More preferably, the active metal oxide sulfur sorbent is also active for removal of sulfur contaminants from heavier FCC product fractions and is added to the FCC catalyst in an amount sufficient to achieve removal of at least about 50 wt.% of sulfur compounds from the FCC naphtha and LCO product fractions, i.e., the FCC liquid product fraction having an FBP of less than about 650°F. In currently preferred embodiments according to this aspect of the invention, the active metal oxide sulfur sorbent is added to the FCC catalyst in an amount of from about 1 to about 10 wt%, based on the weight of the FCC catalyst.

#### BRIEF DESCRIPTION OF THE DRAWINGS

In the drawings which form a portion of the original disclosure of this application:

**Figure 1** is a schematic view of a preferred desulfurization and regeneration process according to the present invention; and

**Figure 2** is a schematic view illustrating an FCC desulfurization process in accordance with another preferred aspect of the present invention.

#### DETAILED DESCRIPTION OF THE INVENTION

The present invention now will be described more fully hereinafter with reference to the accompanying drawings, in which preferred embodiments of the invention are shown. This invention may, however, be embodied in many different forms and should not be construed as limited to the embodiments set forth herein; rather, these embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the scope of the invention to those skilled in the art. Like numbers refer to like elements throughout.

**Figure 1** illustrates a preferred hydrocarbon feedstock desulfurization process according to the present invention. As shown in **Figure 1**, the process includes a desulfurization zone **10** and a regeneration zone **20**. In a preferred process according

to the invention, and illustrated in the drawing, each of the desulfurization zone **10**, and the regeneration zone **20**, is defined by a transport bed reactor. It will be apparent to the skilled artisan however that other conventional fluidized bed reactors, including bubbling bed, circulating bed, and riser reactors can be used in the process of the invention. In addition, the hydrocarbon feedstock desulfurization process of the present invention can be conducted using other conventional catalytic reactors including fixed bed and moving bed reactors, such reactors being well known to those skilled in the art.

Preferred transport bed reactors are similarly known to those skilled in the art and are described in, for example, Campbell, William N. and Henningsen, Gunnar B., *Hot Gas Desulfurization Using Transport Reactors*, publication from the M. W. Kellogg Company, pp 1059-64, 12th Annual International Pittsburgh Coal Conference Proceedings, September 1995, which is incorporated in its entirety herein by reference. Transport bed reactors are also described in U.S. Patent No. 5,447,702, issued on September 5, 1995 to Campbell et al., which is incorporated herein in its entirety by reference.

As illustrated in **Figure 1**, a vaporized sulfur containing hydrocarbon feedstock **30**, which can be FCC naphtha, is fed at a predetermined velocity through an inlet **32** into the desulfurization zone **10** in admixture with a sulfur sorbent comprising an active metal oxide sorbent, or a metal-substituted refractory inorganic oxide cracking catalyst, preferably a sorbent comprising both, i.e., an active metal oxide sorbent supported on, or otherwise combined with a metal-substituted refractory inorganic oxide cracking catalyst. The hydrocarbon feed **30**, including added sorbent, is fed by means of inlet **34** at a temperature between about 300°C (572°F) and about 600°C (1112°F), preferably at a temperature between about 371°C (700°F) and about 538°C (1000°F). Optional hydrogen feed **36** is also introduced into the desulfurization zone **10** via inlet **32**. The combined hydrogen, hydrocarbon and sorbent stream is transported upwardly through a riser pipe **38** during a relatively short time period of less than about 20 seconds, typically less than about 10 seconds for achieving desulfurization of the feed stream **30**. Typically, the superficial gas velocity is between about 5 and about 40 ft/sec, more preferably between about 10 and about 30 ft/sec. The desulfurization zone **10** may have more than one section. In

one of the preferred option, the desulfurization zone **10** will consist of two sections, namely a mixing zone in the bottom and a riser zone at the top. The relative length and diameter of these sections will depend on the kinetics of desulfurization reaction, residence time required, sulfur content of the hydrocarbon feedstock, and feedstock throughput, as will be well known to those skilled in the art.

The hydrocarbon feedstock **30** treated in accordance with the process of the present invention is preferably a normally liquid hydrocarbon fuel or fuel component. The term "normally liquid" means liquid at Standard Temperature and Pressure (STP) conditions as will be apparent to the skilled artisan. Although the feedstock **30** is an FCC naphtha constituting a component or fraction of an automotive gasoline fuel in one preferred embodiment of the invention, the invention is equally applicable to other hydrocarbon fuel feedstocks, and to precursors and components thereof. In particular, the invention is applicable to diesel fuel, aviation fuel, and the like, and to components and precursors thereof including, for example, coker naphthas, thermally cracked naphthas, full-range FCC naphthas, light cycle oils, straight-run distillate fractions, and the like. In this regard, it will be appreciated that the hydrocarbon feedstock **30** supplied to the desulfurization zone **10**, can have differing boiling point ranges, and will contain varying levels of various organic sulfur contaminants typically including organic sulfides and disulfides, mercaptans, substituted and unsubstituted thiophenes, benzothiophenes, and dibenzothiophenes. In the case of FCC naphtha, the concentration of these sulfur compounds depends on boiling point cut from the fractionator and sulfur content of the feed to the FCC, and typically exceeds 150 ppmw, and more typically exceeds 300 ppmw as discussed previously. In the case of diesel fuel components and blends, the sulfur content is typically higher. In particular, diesel is typically formed from a blend comprising light cycle oil recovered from an FCC unit, a distillate recovered from a coker unit (coker distillate), and a straight-run fraction recovered from the crude fractionation unit. Light cycle oils and coker distillates typically have sulfur contents in the range of from about 5,000 to about 30,000 ppmw. Straight-run fractions used in diesel fuels can be derived from sweet or sour crude, and typically have different sulfur content ranges, which in the case of sweet crude straight-run fractions, range from about 300 to about 5,000 ppmw, and in the case of sour crude straight-run fractions, range from about

5000 to about 30,000 ppmw. In turn, the complete diesel fuel blend, prior to a conventional hydrotreating step, typically has a sulfur content of up to about 2000 ppmw, and in some cases can have a sulfur content ranging from about 5000 to about 30,000 ppmw.

The process of the invention is equally applicable to achieve substantial sulfur reduction in partially desulfurized feedstocks such as hydrotreated FCC naphtha and hydrotreated diesel blends and components to reduce their sulfur content to below 30 ppmw, while avoiding olefin saturation, product yield losses and/or increased processing costs which can accompany sulfur removal by HDS processes, particularly in the case of cyclic and polycyclic organic sulfur contaminants. In particular, the desulfurization process of the invention can be employed to accomplish a polishing step or the like for removal of cyclic and polycyclic organic sulfur contaminants from relatively low-sulfur feedstocks, in order to achieve removal of at least about 25 wt.%, more preferably at least about 50 wt.%, of the cyclic and polycyclic organic sulfur contaminants initially present in a low-sulfur hydrocarbon fuel, fuel component or fuel precursor feed.

In embodiments of the invention wherein diesel fuels and/or their components or precursors are treated to reduce sulfur, the preferred process conditions and/apparatus can accordingly be varied depending on the particular feedstock, and sulfur content as will be apparent to those of skill in the art. Thus, when a diesel fuel, or precursor(s) or component(s) thereof, is treated for sulfur removal in the process illustrated in **Figure 1**, a high sulfur diesel feed **30**, is fed in vapor form into the desulfurization zone **10** in admixture with an active metal oxide sorbent at a temperature of between about 350°C (662 °F) and about 750°C (1382°F), preferably at a temperature between about 450°C (842°F) and about 700°C (1292°F). The combined diesel feed and sorbent stream, with or without optional hydrogen feed **36** is transported upwardly through riser pipe **38** during a relatively short residence time of less than about 20 seconds, to thereby achieve desulfurization of the diesel feed **30**.

Although not specifically illustrated in the drawings, the desulfurization process of the invention can be advantageously carried out employing a conventional bubbling bed reactor to accomplish gas-solid contact between the hydrocarbon fuel

feedstock and the active metal oxide sorbent. Bubbling bed reactors can be advantageously employed to treat any of the various fuels, fuel components, and fuel precursors discussed previously, and can be particularly beneficial for treating hydrocarbon fuels and fractions having boiling point ranges exceeding that of FCC naphtha in view of the enhanced gas-solid contact that can be achieved in bubbling bed reactors as compared to transport bed reactors. Bubbling bed reactors provide excellent gas-solid contact and significant process and capital cost benefits as compared to fixed and packed bed reactors which are typically used in prior art hydrodesulfurization processes in order to minimize olefin saturation and product yield losses. The active metal oxide sulfur sorbent employed to treat hydrocarbon feedstocks in bubbling bed reactors according to this embodiment of the invention, is advantageously a high attrition resistance sorbent, discussed in greater detail below. As indicated previously, the desulfurization process of the present invention can alternatively be conducted using other conventional catalytic reactors including fixed bed and moving bed reactors with substantial benefits as compared to prior art hydrodesulfurization processes.

The active metal oxide sulfur sorbent employed in the invention includes at least one active metal oxide capable of removing sulfur compounds from the sulfur-containing fuel feed stream to form a metal sulfide or a metal-sulfur complex. The term "active metal oxide sulfur sorbent" as used herein refers to active metal oxides and mixed active metal oxides, including different oxides of the same elements, for example, zinc titanate which includes various oxides of the formula  $\text{ZnO} \cdot n(\text{TiO}_2)$ , or various iron oxides of the formula  $\text{Fe}_x(\text{O})_y$ , and to mixed oxides of different metals including active metal oxides derived from calcining of active metal oxides, and also to carbonates. Such active metal oxide sorbents can include binders that are mixed or reacted with the active metal oxide, supports that support the metal oxide, and the like as will be apparent to the skilled artisan. Advantageously, the sorbents used in the present invention are regenerable by treatment with oxygen at an elevated temperature. For purposes of the present invention, a sorbent is considered regenerable when it can be used for desulfurization of a hydrocarbon feed, and can thereafter be reactivated at least once by treatment with oxygen at an elevated temperature, to a sulfur removal activity level greater than 50% of the original sulfur

activity level of the sorbent (based on the original weight percent sulfur adsorbing capacity of the sorbent under the same conditions). Active metal oxide sorbents exhibiting good adsorption rates and capacity for sulfur compounds, good regenerability without appreciable loss of efficiency or efficacy, and high attrition resistance are preferred for use in this invention. These sorbents chemically react with the sulfur atoms of the organic sulfur compounds in the feed stream and the active metal oxide is thus converted into a metal sulfide and/or a metal-sulfur complex.

Suitable active metal oxide sorbents for use in the process of the invention, include sorbents based on zinc oxide, zinc titanate, zinc aluminate, zinc silicate, zinc ferrite, iron oxide, iron aluminate, iron zinc oxide, manganese oxide, cerium oxide, copper oxide, copper cerium oxide, copper titanate, copper chromium oxide, copper aluminate, vanadium oxide, calcium oxide, calcium carbonate, magnesium oxide, magnesium carbonate, and mixtures thereof, particularly mixtures of zinc oxides with an iron oxide, and/or copper oxide.

In one particularly preferred embodiment of the invention, the active metal oxide is supported on or otherwise combined with a refractory inorganic oxide cracking catalyst support. Refractory inorganic oxide cracking catalyst support materials are well known to those skilled in the art and include various aluminas, silicas, aluminosilicates, and zeolites. Refractory inorganic oxide cracking catalysts support materials which have been reacted with a metal or metal oxide, such as metal or metal oxide aluminates, metal or metal oxide silicates, metal or metal oxide aluminosilicates, and metal or metal oxide zeolites are currently preferred for use in the present invention. One particularly preferred supported active metal oxide for use in the present invention is a zinc aluminate supported zinc titanate as disclosed in PCT Application WO 99/42201 A1, published August 26, 1999, entitled "Attrition Resistant, Zinc Titanate-Containing, Reduced Sulfur Sorbents", which is hereby incorporated herein by reference. Other metal oxide aluminate supports described in the aforesaid PCT Application are also suitable for use in the present invention. The metal oxide aluminate supported zinc titanate sorbent materials can be formulated to be highly attrition resistant even at high temperatures, while maintaining substantial chemical activity and regenerability. Other metal and metal oxide aluminates such as

iron aluminates, and/or copper aluminates, are also, or alternatively, desirably employed in preferred embodiments of the invention to likewise provide high attrition resistance along with substantial sulfur-removal capacity and good regenerability.

Although the active metal oxide sulfur sorbent is preferably supported by, or combined with, the refractory inorganic oxide cracking catalyst so that the hydrocarbon fuel stream is treated simultaneously by the active metal oxide sorbent and the refractory inorganic oxide cracking catalyst, the present invention also includes processes in which the hydrocarbon fuel stream is treated with the refractory inorganic oxide cracking catalyst and the active metal oxide sorbent sequentially, for example, by passing the hydrocarbon fuel stream through sequential treatment zones including the respective refractory inorganic oxide cracking catalyst and metal oxide sorbent.

Mixed active metal oxide sulfur sorbents are particularly desirable in some advantageous embodiments of the invention. For example, it is known that the sulfur adsorption capabilities of active metal oxide sorbents vary from sorbent to sorbent at different temperatures. It has been found that the reaction kinetics associated with sulfur conversion and sorption by zinc oxide-based sorbents can be substantially enhanced at temperatures below about 525°C (1000°F) by incorporating a minor amount of an active metal sorbent which adsorbs sulfur at lower temperatures than zinc oxide sorbents. One such preferred additional active metal oxide sorbent is copper oxide which may be included in an amount ranging from about 5 to about 45 weight percent, preferably about 5 to about 20 weight percent based on the weight of the active zinc oxide component (for example, zinc titanate). Other promoters may include oxides of iron, silver, gold, or any combination thereof. Other desirable mixed metal oxide sorbents include iron oxides mixed with zinc oxides and/or zinc titanates and/or copper oxides.

Numerous other active metal oxide sorbents can also be used in the process of the invention. Exemplary active metal oxide sorbents are disclosed in U.S. Patent No. 5,254,516, issued October 19, 1993 to Gupta et al., U.S. Patent No. 5,714,431, issued February 3, 1998 to Gupta et al., and U.S. Patent No. 5,972,835, issued October 26, 1999 to Gupta. Still other exemplary active metal oxide sorbents include sorbents which are marketed by Philips Petroleum Company and contain a zinc oxide-based

sorbent (but without any substantial nickel or any other Group 6, 8, 9, or 10 metal other than iron). Other useful metal oxide sorbent materials include those disclosed in U.S. Patent Nos. 5,866,503, 5,703,003, and 5,494,880, issued Feb. 2, 1999, Dec. 30, 1997, and Feb. 27, 1996, respectively, to Siriwardane. The latter are commercially available as RVS materials from SudChemie Inc.

Returning to **Figure 1**, the sorbents fed into the desulfurization zone **10** via inlet pipe **34** are preferably substantially free from active hydrodesulfurization catalysts. The term “active hydrodesulfurization catalyst(s)” is used herein to mean nickel, cobalt, molybdenum, tungsten, and combinations of these metals when present in a state that is chemically active or activatable for hydrodesulfurization. Such metals are considered active or activatable for hydrodesulfurization, in a sulfided state, or in a form that is readily converted to the sulfided metal when exposed to a hydrocarbon feed containing hydrogen and sulfur contaminants at high temperature desulfurizing conditions. In particular, sulfides of nickel, cobalt, molybdenum, tungsten and combinations thereof, are well known by those skilled in the art to be the active catalytic components for hydrodesulfurization. It is likewise well known in the art that oxides of molybdenum, cobalt, nickel, and tungsten can be readily converted to the active sulfides by exposure to hydrogen and sulfur compounds in hydrocarbon feeds at the desulfurization conditions employed in this invention.

Each of the terms, “substantially free” and “substantial absence”, as applied to active hydrodesulfurization catalysts, is used herein to mean that active hydrodesulfurization catalyst(s) are not present, in a form physically accessible to the hydrocarbon feed and in sufficient quantity, to promote substantial conversion of the organic sulfur components in the feedstock into  $H_2S$  by reaction with hydrogen gas, under the desulfurization conditions employed in a process of the invention. In turn, saturation of desirable hydrocarbon olefins in the feed is substantially reduced or eliminated, even in the presence of small quantities of hydrogen, and even at high temperatures. Similarly the costs associated with hydrogen consumption can be greatly reduced or substantially eliminated.

Preferably, the sorbents used in the present invention contain less than about 1.0 wt.% nickel, cobalt, molybdenum, tungsten and/or combinations of these metals, calculated based on the weight of such metal(s), and on the total sorbent weight



including the cracking catalyst support or component. More preferably, the sorbents used in the present invention contain less than about 0.5 wt.% nickel, cobalt, molybdenum, tungsten and/or combinations of these metals, calculated based on the weight of such metal(s), and on the total sorbent weight. Even more preferably the sorbents used in the present invention contain less than about 1.0 wt.% of Group 6 and/or Group 8, 9, and 10 metals (excluding iron), and most preferably the sorbents used in the present invention contain less than about 0.5 wt.% of Group 6 and/or Group 8, 9, and 10 metals (excluding iron), calculated based on the weight of such metal(s), and on the total sorbent weight including the cracking catalyst support or component.

Returning to **Figure 1**, the sorbent added via inlet pipe **34** is transported upwardly through riser pipe **38** and separated via a cyclone separator **42**. The separated sorbent is recovered via a standpipe **44** and a portion of the sorbent is passed via a pipe **46** to the regeneration zone **20** which preferably constitutes a riser pipe **50**. An oxygen-containing regeneration gas **52**, which is preferably ambient air, is added to the riser **50** via inlet pipe **54**. In addition, fresh makeup sorbent **56** is added as necessary via inlet pipe **54**. Further, the metal sulfide additives for enhancing or initiating regeneration, described in the aforementioned Turk et al. U.S. patent, can be advantageously added to the riser **50** via line **58** and inlet **54** in order to improve process economies in the regeneration zone **20** as described in greater detail in the aforementioned Turk et al. patent.

Preferably, the heat carried by the heated sorbent particles admitted to the riser **50** via pipe **46**, and the heat carried by the oxygen in the oxygen-containing stream, are sufficient to establish conditions in the regeneration zone **20** for initiating regeneration of the sulfided active metal oxide sorbent and/or for initiating reaction of the metal sulfide additive, added via line **58**, with oxygen in a highly exothermic combustion reaction to form a metal oxide and sulfur dioxide. The heat released by the metal sulfide additive can, in some cases, be used to initiate regeneration of the active metal oxide sulfur adsorbent at start-up of the process, or can be used as a supplemental heating source for maintaining the desired temperature in the regeneration zone **20**.

The temperature in the regeneration zone during the regeneration reaction typically is within a range of from about the same temperature as the temperature in the desulfurization zone 10 up to a temperature of about 200°C higher than the temperature in zone 10, for example, a temperature of about 425°C (800°F) or higher under steady state conditions. The heat generated during removal of the sulfide contaminants from the active metal oxide sorbents advantageously supplies all or a portion of the heat necessary for vaporization of the hot feed gas stream 30.

In the regeneration zone 20, the oxygen containing regeneration gas reacts with the sulfur on the active metal oxide sorbent to produce sulfur oxides which are removed as a tail gas stream via line 60. Regenerated sorbent is separated via a cyclone separator 62 and passed via a standpipe 64 and inlet pipe 34 back to the desulfurization zone 10.

A desulfurized hydrocarbon fuel stream 70 is recovered from cyclone separator 42 and passed to a conventional separation zone 72 for separation of a recycle hydrogen stream 74 and a desulfurized hydrocarbon fuel stream 76.

The desulfurization process of the present invention can be used to treat naphtha and diesel streams having sulfur contents of from 150 ppmw to over 3,000 ppmw, while reducing the sulfur contaminants by virtually any pre-selected amount. As will be apparent to those skilled in the art, the percentage of sulfur reduction can be readily controlled by varying residence time and temperature in the desulfurization zone.

Advantageously, the process of the invention is conducted at conditions resulting in a sulfur content reduction of at least about 50% or more, preferably at least 80%, more preferably at least about 90%, even more preferably at least about 95%, based on the sulfur content, by weight, of the feedstock. In preferred embodiments of the invention, the sulfur contaminants can be reduced to levels below 20 ppmw, more preferably below 10 ppmw during a residence time preferably below about 20 seconds, more preferably below about 10 seconds. Moreover, such sulfur reductions are preferably achieved with an octane number loss, in the case of FCC naphtha of less than about 5, preferably less than about 2.

With reference now to **Figure 2**, an FCC desulfurization process in accordance with another preferred aspect of the present invention is illustrated by a

schematic view wherein certain of the drawing parts are labeled with the same numbers as in **Figure 1**, and accordingly represent the same parts as the corresponding parts numbered the same in **Figure 1**.

In particular, **Figure 2** illustrates a preferred process of the invention in which sulfur contaminants are removed from an vaporized sulfur-containing FCC feedstock **130** simultaneously with an otherwise conventional FCC process which is conducted in a conventional FCC riser reactor **110** under conventional temperature, pressure and residence times employed for FCC processes. A mixture of a conventional FCC catalyst with a regenerable sorbent comprising an active metal oxide sulfur sorbent supported on, or otherwise combined with a refractory inorganic oxide cracking catalyst, preferably comprising a metal substituent, is fed to the FCC reactor zone **110** via line **140**. Although not specifically shown in **Figure 2**, the FCC catalyst and the regenerable sorbent alternatively can be admitted to the FCC riser **138** via separate lines, or by mixing with the vaporized sulfur-containing FCC feedstock **130**. According to this aspect of the invention, sulfur compounds initially present in the FCC feedstock, or generated during the FCC process, are selectively captured by the sorbent in the FCC riser. The sulfur-laden sorbent is then sent to the FCC regenerator **20** along with the carbon-laden FCC catalyst for regeneration by treatment with an oxygen-containing gas, typically air, which is also used to regenerate the FCC catalyst. During regeneration, sulfur carried by the sorbent is converted to a sulfur dioxide-containing gas stream **60** that can be treated for sulfur removal in a downstream process unit such as a sulfur dioxide scrubber (not shown).

The active metal oxide sulfur sorbent has sufficient sulfur-removal activity, and is added to the FCC reactor **110** in an amount sufficient to achieve removal of at least about 50 wt.% of sulfur contaminants which would otherwise be present in the FCC naphtha product, i.e., the FCC liquid product fraction having an FBP less than about 430°F. Advantageously, the active metal oxide sulfur sorbent is also active for removal of sulfur contaminants from heavier FCC product fractions and is added to the FCC reactor **110** in an amount sufficient to achieve removal of at least about 50 wt.% of sulfur contaminants which would otherwise be present in both of the FCC naphtha and LCO product fractions, i.e., the FCC liquid product fraction having an FBP of less than about 650°F. In currently preferred embodiments according to this

aspect of the invention, the active metal oxide sulfur sorbent is added to the FCC catalyst in an amount of from about 1 to about 10 wt.%, based on the weight of the FCC catalyst.

In more preferred embodiments of this aspect of the invention, the active metal oxide sulfur sorbent has sufficient sulfur-removal activity, and is added to the FCC reactor **110** in an amount sufficient to achieve removal of at least about 50 wt.% of sulfur contaminants which would otherwise be present in the complete liquid product recovered from the FCC reactor. According to still other preferred embodiments, the active metal oxide sulfur sorbent is added to the FCC reactor **110** in an amount sufficient to achieve removal of at least about 75 wt.%, more preferably at least about 90 wt.% of sulfur contaminants which would otherwise be present in the naphtha product. In yet other preferred embodiments, the active metal oxide sulfur sorbent is added to the FCC reactor **110** in an amount sufficient to achieve removal of at least about 75 wt.%, more preferably at least about 90 wt.% of sulfur contaminants which would otherwise be present in both of the FCC naphtha and LCO product fractions.

It has been found that regenerable sorbent comprising an active metal oxide sulfur sorbent supported on, or otherwise combined with a refractory inorganic oxide cracking catalyst are capable of removing thiophenic sulfur compounds in presence of  $\text{H}_2\text{S}$  and mercaptans. Thus, tests have shown that when a mixture of 2,000 ppmv of thiophene and 10,000 ppmv of methyl mercaptan was used to test the performance of one preferred sorbent (see Example 6), it was found that presence of 10,000 ppmv of mercaptan did not affect the activity of the sorbent for thiophene removal. Similar results were also observed when thiophene was mixed with  $\text{H}_2\text{S}$ . This is particularly important in a FCC reactor as about 40 to 50% of the sulfur in the feed to the FCC is converted into  $\text{H}_2\text{S}$ . It has further been found that various preferred sorbents can be successfully regenerated under the conditions used in a typical FCC regenerator without any degradation in catalytic activity. Since the preferred sorbents are extremely attrition-resistant, they can be used along with the FCC catalyst in a conventional FCC process without substantial attrition problems.

One of the added benefits of this aspect of the invention can be increased yield of naphtha and LCO fractions from a FCC system because of change in sulfur

distribution. Currently, refiners typically use a FBP of 410 to 420°F for naphtha from their FCC reactor because they want to limit the sulfur in naphtha, particularly the higher molecular weight sulfur compounds (such as alkyl dibenzothiophenes). Removal of sulfur in the FCC riser itself, in accord with the present invention, can allow this restriction to be eased so that refiners can make premium products at much higher yields than they currently do.

Although the process shown in **Figure 2** achieves desulfurization of an FCC hydrocarbon feed simultaneously with the FCC process, the desulfurization process illustrated in **Figure 2** can alternatively be achieved separately from the FCC process by treating the FCC hydrocarbon feed in a conventional FCC unit, operated at conventional FCC conditions, and positioned upstream of the FCC processing zone.

The following examples illustrate the use of various sorbent compositions for removal of organic sulfur compounds from various simulated syngas and hydrocarbon feedstocks.

#### Example 1

A zinc titanate aluminate sorbent prepared according to Example 8 of PCT Application WO 99/42201 A1, published August 26, 1999, having a weight of about 200g was loaded into a 2 inch ID quartz reactor. This reactor was sealed in a stainless steel pressure shell. The system was pressurized to 50 psig and heated to 1000 °F in 4 SLPM (standard liters per minute) of nitrogen. The reactor effluent was used to continuously purge a sample loop for a Varian 3300 Gas Chromatograph fitted with a Sievers Model 355 sulfur chemiluminescence detector capable of detecting below 200 ppbv (parts per billion, volume) of sulfur.

The test was started by adjusting the flow to the reactor to 2 SLPM of hydrogen and 2 SLPM of a nitrogen mixture containing 200 ppmv (parts per million volume) each of ethyl-, propyl-, and butyl-mercaptan. At this time, HP ChemStation software was used to start a sequence designed to sample the reactor effluent at intervals of about 6 minutes. After 120 minutes, the flow was adjusted to have 0.4 SLPM of hydrogen and 3.6 SLPM of the nitrogen and mercaptan mixture. At a total run time of 240 minutes the flow was changed to 0.8 SLPM of 10 vol% H<sub>2</sub>S in hydrogen and 3.2 SLPM of nitrogen. When the level of H<sub>2</sub>S in the reactor effluent reached 100 ppmv, the sulfidation was terminated.

While purging the sulfidation gases of the reactor for about 30 minutes with 4 SLPM nitrogen, the sorbent was heated to 1150°F. After the reactor had been purged and the temperature had stabilized at the new temperature, the sorbent was regenerated with 4 SLPM of air. The regeneration was monitored by the SO<sub>2</sub> and O<sub>2</sub> leak in the reactor effluent. When the O<sub>2</sub> level had increased above 5 vol% and the SO<sub>2</sub> concentration had dropped below 2,000 ppmv (parts per million, volume), the regeneration was stopped.

In preparation for the next sulfidation, the sorbent bed was cooled to 1000 °F. Sulfidation was started with a mixture of 3.6 SLPM of hydrogen, 0.2 SLPM of 1,960 ppmv thiophene in nitrogen and 0.25 SLPM of nitrogen. At the start of sulfidation, the HP ChemStation software sequence analyzing the reactor effluent every 6 minutes was also started. The flows were changed to 3.6 SLPM of hydrogen, 1 SLPM of the 1,960 ppmv thiophene in nitrogen mixture and 0.25 SLPM of nitrogen after 120 min. These flow conditions were maintained for another 120 minutes. The next set of flow conditions were 0.4 SLPM of 10 vol% H<sub>2</sub>S in hydrogen, 3.6 SLPM of hydrogen and 0.25 SLPM of nitrogen. These conditions were maintained until the H<sub>2</sub>S concentration in the effluent exceeded 100 ppmv.

For regeneration, the sorbent bed was heated to 1150°F. The regeneration was started with 4 SLPM of air. Regeneration was stopped when the effluent SO<sub>2</sub> concentration dropped below 2,000 ppmv and the effluent O<sub>2</sub> concentration increased above 5 vol%.

For the third sulfidation, the temperature in the sorbent bed was dropped to 1000°F. For the first 120 minutes of sulfidation, the flows were 3.6 SLPM of hydrogen, 0.2 SLPM of 945 ppmv 2-ethyl thiophene in nitrogen and 0.3 SLPM of nitrogen. After 120 minutes, the flows were changed to 3.6 SLPM of hydrogen, 1.0 SLPM of 945-ppmv thiophene in nitrogen, and 0.3 SLPM of nitrogen. The sulfidation and, consequently, the test were then terminated. The comparison of the steady state feed and effluent concentration for the various sulfur compounds (mercaptans, thiophene and ethyl thiophene) are listed in Table 1.

**Table 1. Comparison Of The Concentration Of The Sulfur Contaminant In The Reactor Feed And Effluent With Zinc Titanate Aluminate Sorbent**

Compound	Concentration (ppmv)	
	Feed	Effluent
Mercaptan (Ethyl-, propyl- and butyl-)	300	0.5
Mercaptan (Ethyl-, propyl- and butyl-)	540	1
Thiophene	100	1
Thiophene	400	5
2-Ethylthiophene	60	0.5
2-Ethylthiophene	200	2

### Example 2

The following testing sequence was used to screen the following sorbent materials (1) the zinc titanate aluminate of Example 1, (2) a zinc aluminate (prepared as set forth below), (3) alumina (commercially available), (4) zinc titanate, (5) a physical mixture of zinc titanate and alumina, (6) a physical mixture of zinc aluminate and zinc titanate, (7) a commercial, stabilized zinc oxide guard bed material, G72D, commercially available from Sud-Chemie Inc, and (8) ECAT, a silica based commercial FCC catalyst. The test began by loading 50g of each sample into an 1 inch ID quartz reactor. The reactor was placed in a furnace with temperature control based on the temperature at the center of the sorbent bed. The quartz reactor was fitted with two feed inlets, a thermocouple well and effluent side arm. The reactor effluent was setup to continuously feed the sample loop of a Hewlett Packard (HP) 6890 GC fitted with a J&W GS GasPro column and a Sievers Model 355 sulfur chemiluminescence detector. This detector can easily detect sulfur concentrations to below 200 ppbv.

In preparation for the run, the sorbent bed was heated to 800°F in a nitrogen flow of approximately 500 sccm. The test was started by introducing into the reactor a mixture of 2,100 ppmv thiophene and nitrogen at 50 sccm (standard cubic centimeters per minute) with 400 sccm of nitrogen. HP ChemStations software was used to sample the reactor effluent periodically. The reactor effluent was monitored until two to three sequential results indicated steady state operation had been achieved. This typically took between 40 to 60 minutes. At this point the reactor system was bypassed and the reactor feed was fed directly to the GC system for analysis. As with the reactor effluent, the reactor feed was analyzed until several

sequential results indicated the sulfur concentrations were consistent. The results from these screening tests are shown in Table 2.

The zinc aluminate sample used in these tests was prepared by mixing 66.9 g of alumina (Engelhard) and 53.4 g of zinc oxide (Aesar) in 300 ml of deionized (DI) water. This slurry was gently heated with continuous stirring for 1 hour. The slurry was dried at 120°C overnight and calcined at 800°C for 6 hours.

The effect of hydrogen addition was demonstrated in repeat test for alumina. During this test, the flows were set to 450 sccm of hydrogen and 50 sccm of a 2,100 ppmv thiophene in nitrogen mixture. The results for both the test with hydrogen and without hydrogen can be seen in Table 2.

**Table 2. Comparison of Thiophene Concentration in the Reactor Feed and Effluent for Catalyst/Sorbent Screening Test**

Material	Feed Gas Composition			Effluent
	N <sub>2</sub>	H <sub>2</sub>	Thiophene	Thiophene
	(Vol%)	(vol%)	(ppmv)	(ppmv)
Zinc titanate	Balance		137	114
Zinc aluminate	Balance		205	0.09
Alumina	Balance		238	23
Alumina	Balance	90.0	146	0.148
Zinc titanate (40 wt%) and Zinc aluminate (60 wt%)	Balance		215	0.07
Zinc titanate (40 wt%) and alumina (60 wt%)	Balance		195	82
Zinc titanate aluminate	Balance		132	0.115
ECAT	Balance		919	600
G72D (zinc oxide)	Balance		133	0.78

As can be seen in Table 2, the zinc aluminate was effective for removal of the cyclic sulfur compositions with and without added or reacted zinc titanate. Moreover, the zinc aluminate was more effective without any hydrogen addition in removing the



sulfur compounds than alumina with hydrogen. The zinc titanate aluminate was similarly effective.

### Example 3

This example used the same microreactor system that was used in Example 2. An isooctane sample spiked with various sulfur compounds was used to mimic FCC naphtha (shown in Table 3). Tests were conducted with this mixture to determine the effectiveness of the zinc titanate aluminate sorbent used in Example 1 at 1,000°F with and without H<sub>2</sub>. The results are shown in Table 3.

**Table 3. Removal Of Various Sulfur Compounds From A Simulated Isooctane Sample Using Zinc Titanate Aluminate Sorbent With And Without Hydrogen**

Sulfur Compound	Feed (ppmw)	Product (ppmw)	
		Test 1	Test 2
		Without H <sub>2</sub>	With H <sub>2</sub>
Ethyl Mercaptan	159.8	0.0	0.0
Carbon Disulfide	217.7	4.7	0.0
Isopropyl Mercaptan	103.0	0.0	0.0
Thiophene	88.5	46.6	33.6
Diethyl Sulfide	74.1	4.3	0.0
2-Ethyl Thiophene	62.0	54.7	43.6
Diethyl Disulfide	105.1	6.6	0.8
Benzothiophene	39.8	89.8	58.3
Dibenzothiophene	27.7	2.9	13.3
<b>TOTAL</b>	<b>877.8</b>	<b>209.6</b>	<b>149.6</b>
<b>% Removal</b>		<b>76.1</b>	<b>82.9</b>

Although not shown in Table 3, in each case the effluent was monitored for H<sub>2</sub>S, and no traces were found in any of the tests. As seen in Table 3, even though no hydrodesulfurization catalyst was used in any of these tests, addition of H<sub>2</sub> improved the extent of desulfurization from 76.1 to 82.9 percent, with significant increase in removal of benzothiophene and dibenzothiophene. Although not fully understood, this is believed due to the enhanced stabilization of hydrocarbon radicals resulting from ring cracking, which in turn, is believed to decrease or minimize deactivation of the sorbent, e.g., by coking. Further, it is to be noted that the sorbent has a surface area of about 5 m<sup>2</sup>/g, and that higher surface areas should improve the desulfurization efficiency.

#### Example 4

Example 3 was repeated except that the reaction temperature was lowered to 800°F and the zinc titanate aluminate sorbent was modified to include a copper promoter using the following procedure.

100g of the zinc titanate aluminate sorbent powder of Example 3 was dried at 120°C for one hour and then cooled in a desiccator.

To 35 mL D.I. H<sub>2</sub>O in a 100 ml beaker was added 28.8 g of cupric nitrate (obtained from Sigma Chemical). 5.5 mL of the Cu(NO<sub>3</sub>)<sub>2</sub> solution was applied to the zinc titanate aluminate sorbent powder drop by drop while stirring with a Teflon rod. The resultant powder was calcined at 200°C (5°C/min) for 2 hours and cooled in a desiccator. The impregnation and calcining steps were repeated to achieve a second impregnation. The twice impregnated sorbent was dried at 120°C overnight, and then calcined at 280°C (5°C/min) for 4 hours.

The results of testing of this Cu-impregnated sorbent are shown in Table 4. As can be seen from these results, the copper promoter allowed the same sulfur removal efficiency at 800°F as was achieved with unpromoted zinc titanate aluminate at 1000°F.

**Table 4. Removal Of Various Sulfur Compounds With And Without The Addition Of The Copper Promoter To The Zinc Titanate Aluminate Sorbent**

Sulfur Compound	Feed (ppmw)	Product (ppmw)	
		Test 1	Test 2
		1,000°F (original sorbent)	800°F (modified sorbent)
Ethyl Mercaptan	159.8	0.0	0.0
Carbon Disulfide	217.7	0.0	0.0
Isopropyl Mercaptan	103.0	0.0	0.0
Thiophene	88.5	33.6	54.6
Diethyl Sulfide	74.1	0.0	175.8
2-Ethyl Thiophene	62.0	43.6	0.0
Diethyl Disulfide	105.1	0.8	0.0
Benzothiophene	39.8	58.3	0.0
Dibenzothiophene	27.7	13.3	0.0
<b>TOTAL</b>	<b>877.8</b>	<b>149.6</b>	<b>280.4</b>
<b>% Removal</b>		<b>82.9</b>	<b>73.7</b>

## Example 5

The following testing sequence was used to screen the following sorbent materials: (1) Iron Oxide supported on the Zinc Titanate Aluminate of Example 1 (prepared as described below); (2) Zinc Aluminate prepared as described in Example 2; (3) Copper Oxide supported on Zinc Aluminate, (prepared as described below); and, (4) Iron Oxide supported on Zinc Aluminate, (prepared as described below).

Preparation of sorbent (1), Iron Oxide supported on Zinc Titanate Aluminate.

A 100g sample of the zinc titanate aluminate from Example 1 was dried at 120°C for an hour and allowed to cool in a desiccator. A solution of iron nitrate was prepared by dissolving 38.3g of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in 20 ml of deionized (DI) water. A total of 15 ml of this iron nitrate solution was added to the zinc titanate aluminate drop by drop while continuously mixing the zinc titanate aluminate. The resulting powder was calcined at 200°C for 2 hours and cooled in a desiccator. A second sample of iron nitrate solution was made and impregnated on the previously impregnated zinc titanate aluminate in the manner described above. The final impregnated sample was dried at 120°C overnight and calcined at 280°C for 4 hours.

Preparation of sorbent (3), Copper Oxide supported on Zinc Aluminate.

A 100 g sample of the zinc aluminate from Example 2 was treated with a copper impregnating solution prepared by dissolving 44.9 g of  $\text{Cu}(\text{NO}_3)_2$  in 55 ml of DI water. During the first impregnation 26 ml of the copper impregnating solution was added to the zinc aluminate drop by drop as the zinc aluminate was vigorously stirred. The sample was then dried at 200°C for 2 hours and cooled in a desiccator. After cooling, the sample was impregnated with another 26 ml of the copper impregnating solution in the manner described above. The sample was dried at 120°C and calcined for 4 hours at 280°C.

Preparation of sorbent (4), Iron Oxide supported on Zinc Aluminate.

An iron impregnated zinc aluminate sample was prepared using the same procedure as used for the copper impregnated zinc aluminate of sorbent (3) above. The iron impregnating solution was prepared by dissolving 76.2g of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in 40 ml of DI water. The twice impregnated sample was dried and calcined in a like manner as sorbent (3) above

The test began by loading 50 g of each sample into a 1-inch ID quartz reactor. The reactor was placed in a furnace with temperature control based on the temperature at the center of the sorbent bed. The quartz reactor was fitted with two feed inlets, a thermocouple well, and an effluent side arm. The reactor effluent was setup to continuously feed the sample loop of a HP 6890 GC fitted with a J&W GC GasPro column and a Sievers Model 355 sulfur chemiluminescence detector. This detector can easily detect sulfur down to 50 ppbv.

In preparation for each test, the sorbent bed was heated to 800°F in a nitrogen flow of approximately 500 sccm. The test was started by introducing into the reactor a mixture containing 200 ppmv methylmercaptan, and 200 ppmv thiophene with the balance being nitrogen. HP Chemstations software was used to sample the reactor effluent periodically. The reactor effluent was monitored until two or three sequential results indicated steady state operation had been achieved. This typically took between 40 to 60 minutes. At this point the reactor system was bypassed and the reactor feed was feed directly to the GC system for analysis. As with the reactor effluent, the reactor feed was analyzed until several sequential results indicated the sulfur concentrations were consistent. The results from these screening tests are shown in Table 5.

**Table 5. Comparison of Reactor Feed and Effluent  
For Second Sorbent Screening Test**

Sorbent Material	Methyl Mercaptan (ppmv)		Thiophene (ppmv)	
	Feed	Effluent	Feed	Effluent
Iron Oxide/Zinc Titanate Aluminate	186	N.D.*	274	N.D.
Zinc aluminate	191	N.D.	281	0.7
Copper Oxide/Zinc Aluminate	191	N.D.	290	N.D.
Iron Oxide/Zinc Aluminate	191	N.D.	291	0.2

\* Not Detected

#### Example 6

A 50g sample of the Zinc Aluminate-supported Iron Oxide sorbent prepared as described in Example 5 was loaded in the 1-inch ID quartz reactor. The furnace heating was controlled with a thermocouple in the sorbent bed approximately 1-in from the quartz frit supporting the sorbent bed. After installing the quartz reactor and connecting the feed and effluent lines, the sorbent bed was heated to 800°F in a

nitrogen flow of approximately 500 sccm. When the sorbent bed temperature was 800°F, the sorbent was exposed to 500 sccm of air for 60 min. The reactor was purged with nitrogen at 500 sccm for 15 min to remove any traces of oxygen. The sample was then exposed to a mixture with 1920 ppmv of thiophene and 9940 ppmv methyl mercaptan in nitrogen at 500 sccm. HP Chemstations software was used to periodically record the sulfur content of the reactor effluent as determined by an HP 6890 GC equipped with a J&W GasPro column and Sievers Model 355 sulfur chemiluminescence detector. Exposure of the sorbent sample continued until the thiophene concentration in the effluent increased to 100 ppmv. At this point no methyl mercaptan was detected in the effluent. The total time of sorbent exposure prior to breakthrough (thiophene effluent concentration > 100 ppmv) was 5 hours. This corresponds to a sulfur weight loading of 4.4 wt % for the methyl mercaptan and 0.7 wt% for the thiophene.

The sorbent sample was then regenerated with 500 sccm of air at 800°F for 60 min. The sorbent was exposed to the same methyl mercaptan, thiophene and nitrogen mixture at the same conditions as during the first exposure to breakthrough. The total exposure time prior to breakthrough for this second exposure was 4 hours. Once again the thiophene effluent concentration was observed to increase to 100 ppmv without any methyl mercaptan being detected. The sulfur loadings were 0.84 wt% for thiophene and 3.6 wt% for methyl mercaptan.

The sorbent was again regenerated with 500 sccm of air at 800°F for 120 min. After purging of the oxygen by nitrogen, the sorbent was exposed to a 1970 ppmv thiophene in nitrogen mixture at 500 sccm at 800°F. The effluent sulfur content was monitored as in previous exposure cycles. The sorbent was exposed to this mixture for 6 hours. The test had to be terminated at this point because the tank with the thiophene/nitrogen mixture was empty. The effluent thiophene concentration at this time was 56 ppmv. Thus, breakthrough had not been reached. The sulfur loading for this exposure test was 1 wt% for thiophene.

Many modifications and other embodiments of the invention will come to mind to one skilled in the art to which this invention pertains having the benefit of the teachings presented in the foregoing descriptions and the associated drawing.

Therefore, it is to be understood that the invention is not to be limited to the specific embodiments disclosed and that modifications and other embodiments are intended to be included within the spirit and scope of the appended claims. Although specific terms are employed herein, they are used in a generic and descriptive sense only and not for purposes of limitation.

THAT WHICH IS CLAIMED:

1. A process for removing sulfur compounds from a normally liquid hydrocarbon fuel or fuel component feedstock having a sulfur content of at least about 150 ppmw comprising the steps:

contacting the feedstock in the substantial absence of a hydrodesulfurization catalyst, with a regenerable sorbent material comprising at least one active metal oxide sorbent capable of selectively removing sulfur compounds present in the hydrocarbon feedstock and a refractory inorganic oxide cracking catalyst capable of cracking cyclic organic sulfur compounds; and

recovering a hydrocarbon product having a sulfur content of about 50% or less than the sulfur content of the feedstock.

2. The process of Claim 1, further comprising regenerating at least a portion of said sorbent with an oxidizing gas under conditions sufficient to convert metal sulfide into said metal oxide sorbent and thereby provide regenerated sorbent, and recycling at least a portion of said regenerated sorbent to said contacting step.

3. The process of Claim 1, wherein said refractory inorganic oxide cracking catalyst comprises at least one metal-substituted refractory inorganic oxide cracking catalyst, said metal being the same metal as the metal of said active metal oxide sorbent.

4. The process of Claim 1, wherein said contacting step is conducted at a temperature of at least about 300°C.

5. The process of Claim 1, wherein said hydrocarbon feedstock comprises at least about 100 ppmw of cyclic organic sulfur compounds.

6. The process of Claim 5, wherein said wherein said hydrocarbon feedstock comprises a sulfur content of at least about 300 ppmw.

7. The process of Claim 1 wherein said contacting step is conducted such that said feedstock is contacted simultaneously with said sorbent and said refractory inorganic oxide cracking catalyst.

8. The process of Claim 2, further comprising regenerating at least a portion of said refractory inorganic oxide cracking catalyst with an oxidizing gas under conditions sufficient to remove sulfur from said refractory inorganic oxide cracking catalyst and thereby provide regenerated refractory inorganic oxide cracking catalyst, and recycling at least a portion of said regenerated refractory inorganic oxide cracking catalyst to said contacting step.

9. The process of Claim 1, wherein said hydrocarbon feedstock comprises FCC naphtha.

10. The process of Claim 1, wherein said hydrocarbon feedstock consists essentially of FCC naphtha.

11. The process of Claim 9, wherein said hydrocarbon product recovered in said recovering step has a sulfur content of less than about 10 ppmw.

12. The process of Claim 1, wherein said hydrocarbon feedstock comprises diesel fuel or a precursor or component thereof.

13. The process of Claim 12, wherein said hydrocarbon feedstock comprises coker naphtha, thermally cracked naphtha, light cycle oil, or a straight-run diesel fraction.

14. The process of Claim 1, wherein said metal oxide sorbent comprises zinc oxide.

15. The process of Claim 1, wherein said refractory inorganic oxide cracking catalyst comprises alumina or a metal-substituted alumina.

16. The process of Claim 1, wherein said metal oxide sorbent comprises metal oxide sorbent and said refractory inorganic oxide cracking catalyst comprise zinc oxide and zinc aluminate.

17. The process of Claim 1, wherein said contacting step is carried out in a transport bed reactor with a vapor residence time of less than about 20 seconds.

18. A process for removing cyclic and polycyclic organic sulfur compounds from a normally liquid hydrocarbon feedstock comprising the steps:  
contacting the feedstock in the substantial absence of a hydrodesulfurization catalyst, with a sorbent comprising a metal-substituted refractory inorganic oxide cracking catalyst capable of cracking cyclic organic sulfur compounds, said metal being selected from the group consisting of metals which are capable in their oxide form, of adsorption of reduced sulfur compounds by conversion of the metal oxide to a metal sulfide; and

recovering a hydrocarbon product having a cyclic and polycyclic organic sulfur content at least about 25% less than the cyclic and polycyclic organic sulfur content of the feedstock, based the sulfur weight of said cyclic and polycyclic organic sulfur compounds in said feedstock and the sulfur weight of cyclic and polycyclic organic sulfur compounds in said product.

19. The process of Claim 18, further comprising regenerating at least a portion of said sorbent with an oxidizing gas under conditions sufficient to convert metal sulfide into said metal oxide and thereby provide regenerated sorbent, and recycling at least a portion of said regenerated sorbent to said contacting step.



20. The process of Claim 18, wherein said sorbent further comprises an active metal oxide sorbent capable of selectively removing sulfur compounds present in the hydrocarbon feedstock, the metal of said metal oxide being the same metal as the metal of said metal-substituted refractory inorganic oxide cracking catalyst sorbent.

21. The process of Claim 18, wherein said contacting step is conducted at a temperature of at least about 300°C.

22. The process of Claim 18, wherein said hydrocarbon feedstock comprises at least about 150 ppmw of sulfur compounds.

23. The process of Claim 18, wherein said product has a sulfur content at least about 50% less than the sulfur content of the feedstock.

24. The process of Claim 23, wherein said hydrocarbon feedstock comprises FCC naphtha.

25. The process of Claim 18, wherein said hydrocarbon feedstock comprises FCC naphtha.

26. The process of Claim 23, wherein said hydrocarbon feedstock consists essentially of FCC naphtha.

27. The process of Claim 18, wherein said hydrocarbon feedstock consists essentially of FCC naphtha.

28. The process of Claim 24, wherein said hydrocarbon product has a sulfur content of less than about 10 ppmw.

29. The process of Claim 18, wherein said hydrocarbon feedstock comprises diesel fuel or a precursor or component thereof.

30. The process of Claim 18, wherein said hydrocarbon feedstock consists essentially of diesel fuel or a precursor or component thereof

31. The process of Claim 29, wherein said hydrocarbon feedstock comprises coker naphtha, thermally cracked naphtha, light cycle oil, or a straight-run diesel fraction.

32. The process of Claim 30, wherein said hydrocarbon feedstock comprises coker naphtha, thermally cracked naphtha, light cycle oil, or a straight-run diesel fraction.

33. The process of Claim 18, wherein said metal-substituted refractory inorganic oxide cracking catalyst comprises zinc aluminate.

34. The process of Claim 20, wherein said metal-substituted refractory inorganic oxide cracking catalyst comprises zinc aluminate.

35. The process of Claim 20, wherein said active metal oxide sorbent comprises zinc oxide.

36. The process of Claim 28, wherein said active metal oxide sorbent comprises zinc titanate.

37. The process of Claim 18, wherein said metal-substituted refractory inorganic oxide cracking catalyst comprises iron aluminate.

38. The process of Claim 20, wherein said metal-substituted refractory inorganic oxide cracking catalyst comprises iron aluminate.

39. The process of Claim 20, wherein said active metal oxide sorbent comprises an iron oxide.

40. The process of Claim 18, wherein said contacting step is carried out in a transport bed reactor with a vapor residence time of less than about 20 seconds.

41. The process of Claim 18, wherein said contacting step is carried out in a bubbling bed reactor.

42. The process of Claim 20, wherein said contacting step is carried out in a transport bed reactor with a vapor residence time of less than about 20 seconds.

43. The process of Claim 20, wherein said contacting step is carried out in a bubbling bed reactor.

44. The process of Claim 24, wherein said contacting step is carried out in a transport bed reactor with a vapor residence time of less than about 20 seconds.

45. The process of Claim 24, wherein said contacting step is carried out in a bubbling bed reactor.

46. The process of Claim 29, wherein said contacting step is carried out in a transport bed reactor with a vapor residence time of less than about 20 seconds.

47. The process of Claim 29, wherein said contacting step is carried out in a bubbling bed reactor.

48. A process for removing cyclic and polycyclic organic sulfur compounds from a normally liquid hydrocarbon feedstock comprising the steps:  
contacting the feedstock in the substantial absence of a hydrodesulfurization catalyst, with a sorbent comprising at least one active metal oxide sorbent capable of selectively removing sulfur compounds present in the hydrocarbon feedstock and a

refractory inorganic oxide cracking catalyst capable of cracking cyclic organic sulfur compounds; and

recovering a hydrocarbon product having a cyclic and polycyclic organic sulfur content at least about 25% less than the cyclic and polycyclic organic sulfur content of the feedstock, based the sulfur weight of said cyclic and polycyclic organic sulfur compounds in said feedstock and the sulfur weight of cyclic and polycyclic organic sulfur compounds in said product.

49. The process of Claim 48, further comprising regenerating at least a portion of said sorbent with an oxidizing gas under conditions sufficient to convert metal sulfide into said metal oxide and thereby provide regenerated sorbent, and recycling at least a portion of said regenerated sorbent to said contacting step.

50. The process of Claim 48, wherein said contacting step is conducted at a temperature of at least about 300°C.

51. The process of Claim 48, wherein said hydrocarbon feedstock comprises at least about 150 ppmw of sulfur compounds.

52. The process of Claim 48, wherein said product has a sulfur content at least about 50% less than the sulfur content of the feedstock.

53. The process of Claim 52, wherein said hydrocarbon feedstock comprises FCC naphtha.

54. The process of Claim 48, wherein said hydrocarbon feedstock comprises hydrotreated FCC naphtha.

55. The process of Claim 48, wherein said hydrocarbon feedstock comprises hydrotreated diesel fuel or a hydrotreated precursor or hydrotreated component thereof.

56. The process of Claim 48, wherein said hydrocarbon feedstock consists essentially of a hydrotreated gasoline or diesel fuel or a hydrotreated precursor or hydrotreated component of gasoline or diesel fuel.

57. The process of Claim 56, wherein said hydrocarbon product has a sulfur content of less than about 10 ppmw.

58. The process of Claim 48, wherein said hydrocarbon feedstock comprises diesel fuel or a precursor or component thereof.

59. The process of Claim 48, wherein said hydrocarbon feedstock consists essentially of diesel fuel or a precursor or component thereof

60. The process of Claim 59, wherein said hydrocarbon feedstock comprises coker naphtha, thermally cracked naphtha, light cycle oil, or a straight-run diesel fraction.

61. The process of Claim 52, wherein said hydrocarbon feedstock comprises coker naphtha, thermally cracked naphtha, light cycle oil, or a straight-run diesel fraction.

62. The process of Claim 48, wherein said refractory inorganic oxide cracking catalyst comprises zinc aluminate.

63. The process of Claim 48, wherein said refractory inorganic oxide cracking catalyst comprises iron aluminate.

64. The process of Claim 48, wherein said active metal oxide sorbent comprises zinc oxide.

65. The process of Claim 48, wherein said active metal oxide sorbent comprises an iron oxide.

66. The process of Claim 48, wherein said contacting step is carried out in a transport bed reactor with a vapor residence time of less than about 20 seconds.

67. The process of Claim 48, wherein said contacting step is carried out in a bubbling bed reactor.

68. The process of Claim 52, wherein said contacting step is carried out in a transport bed reactor with a vapor residence time of less than about 20 seconds.

69. The process of Claim 52, wherein said contacting step is carried out in a bubbling bed reactor.

70. A process for removing sulfur compounds from a normally liquid hydrocarbon fuel or fuel component feedstock having a sulfur content of at least about 150 ppmw comprising the steps:

contacting the feedstock in a transport bed reactor during a vapor residence time of less than about 20 seconds, with a regenerable sorbent material comprising at least one active metal oxide sorbent capable of selectively removing sulfur compounds present in the hydrocarbon feedstock and a refractory inorganic oxide cracking catalyst capable of cracking cyclic organic sulfur compounds, said reactor being substantially free of hydrodesulfurization catalyst; and

recovering a hydrocarbon product having a reduced sulfur content.

71. The process of Claim 70, further comprising regenerating at least a portion of said sorbent with an oxidizing gas under conditions sufficient to convert metal sulfide into said metal oxide sorbent and thereby provide regenerated sorbent, and recycling at least a portion of said regenerated sorbent to said contacting step.

72. The process of Claim 70, wherein said refractory inorganic oxide cracking catalyst comprises at least one metal-substituted refractory inorganic oxide

cracking catalyst, said metal being the same metal as the metal of said active metal oxide sorbent.

73. The process of Claim 70, wherein said contacting step is conducted at a temperature of at least about 300°C.

74. The process of Claim 70, wherein said hydrocarbon feedstock comprises at least about 100 ppmw of cyclic and polycyclic organic sulfur compounds.

75. The process of Claim 70, wherein said wherein said hydrocarbon feedstock comprises a sulfur content of at least about 300 ppmw.

76. The process of Claim 70 wherein said contacting step is conducted such that said feedstock is contacted simultaneously with said sorbent and said refractory inorganic oxide cracking catalyst.

77. The process of Claim 72, further comprising regenerating at least a portion of said refractory inorganic oxide cracking catalyst with an oxidizing gas under conditions sufficient to remove sulfur from said refractory inorganic oxide cracking catalyst and thereby provide regenerated refractory inorganic oxide cracking catalyst, and recycling at least a portion of said regenerated refractory inorganic oxide cracking catalyst to said contacting step.

78. The process of Claim 70, wherein said hydrocarbon feedstock comprises FCC naphtha.

79. The process of Claim 70, wherein said hydrocarbon feedstock comprises diesel fuel or a precursor or component thereof.

80. The process of Claim 70, wherein said hydrocarbon product recovered in said recovering step has a sulfur content of less than about 10 ppmw.

81. The process of Claim 70, wherein said metal oxide sorbent comprises zinc oxide.

82. The process of Claim 70, wherein said refractory inorganic oxide cracking catalyst comprises alumina or a metal-substituted alumina.

83. The process of Claim 70, wherein said metal oxide sorbent comprises an iron oxide.

84. The process of Claim 70, wherein said refractory inorganic oxide cracking catalyst comprises iron aluminate.

85. A process for removing cyclic and polycyclic organic sulfur compounds from a normally liquid hydrocarbon feedstock having a sulfur content comprising at least about 100 ppmw of cyclic and polycyclic organic sulfur compounds comprising the steps:

contacting the feedstock in a transport bed reactor during a vapor residence time of less than about 20 seconds with a sorbent comprising a metal-substituted refractory inorganic oxide cracking catalyst capable of cracking cyclic organic sulfur compounds, said metal being selected from the group consisting of metals which are capable in their oxide form, of adsorption of reduced sulfur compounds by conversion of the metal oxide to a metal sulfide, said reactor being substantially free of hydrodesulfurization catalyst; and

recovering a hydrocarbon product having a cyclic and polycyclic organic sulfur content at least about 25% less than the cyclic and polycyclic organic sulfur content of the feedstock, based the sulfur weight of said cyclic and polycyclic organic sulfur compounds in said feedstock and the sulfur weight of cyclic and polycyclic organic sulfur compounds in said product.

86. The process of Claim 85, further comprising regenerating at least a portion of said sorbent with an oxidizing gas under conditions sufficient to convert



metal sulfide into said metal oxide and thereby provide regenerated sorbent, and recycling at least a portion of said regenerated sorbent to said contacting step.

87. The process of Claim 85, wherein said sorbent further comprises an active metal oxide sorbent capable of selectively removing sulfur compounds present in the hydrocarbon feedstock, said metal being the same metal as the metal of said metal-substituted refractory inorganic oxide cracking catalyst sorbent.

88. The process of Claim 85, wherein said contacting step is conducted at a temperature of at least about 300°C.

89. The process of Claim 85, wherein said hydrocarbon feedstock comprises at least about 300 ppmw of sulfur compounds.

90. The process of Claim 86, wherein said wherein said product has a sulfur content at least about 50% less than the sulfur content of the feedstock.

91. The process of Claim 85, wherein said hydrocarbon feedstock comprises an FCC naphtha.

92. The process of Claim 85, wherein said hydrocarbon feedstock comprises diesel fuel or a precursor or component thereof.

93. The process of Claim 85, wherein said hydrocarbon product recovered in said recovering step has a sulfur content of less than about 10 ppmw.

94. The process of Claim 87, wherein said metal oxide sorbent comprises zinc oxide.

95. The process of Claim 85, wherein said metal-substituted refractory inorganic oxide cracking catalyst comprises a metal-substituted alumina.

96. The process of Claim 87, wherein said metal oxide sorbent comprises an iron oxide.

97. The process of Claim 85, wherein said metal-substituted refractory inorganic oxide cracking catalyst comprises iron aluminate.

98. A process for removing organic sulfur compounds from an FCC hydrocarbon stream during an FCC process comprising the steps:

contacting an FCC hydrocarbon feedstock in a reaction zone under FCC reaction conditions with an FCC catalyst and a regenerable sorbent comprising an active metal oxide sulfur sorbent supported on or otherwise combined with a refractory inorganic oxide cracking catalyst, said metal being selected from the group consisting of metals which are capable in their oxide form, of adsorption of reduced sulfur compounds by conversion of the metal oxide to a metal sulfide; and

recovering a cracked hydrocarbon product comprising FCC naphtha having a sulfur content at least about 50 wt.% less than the sulfur content of said FCC naphtha when said FCC process is conducted without said regenerable sorbent under substantially identical FCC reaction conditions.

99. The process of Claim 98, further comprising regenerating at least a portion of said sorbent and said FCC catalyst with an oxidizing gas under FCC catalyst regenerating conditions to thereby remove sulfur from said sorbent and thereby regenerate said sorbent and said FCC catalyst, and recycling at least a portion of the regenerated sorbent and regenerated FCC catalyst said to said contacting step.

100. The process of Claim 98 wherein said cracked hydrocarbon product recovered in said recovering step comprises FCC naphtha and light cycle oil fractions having a sulfur content at least about 50 wt.% less than the sulfur content of said FCC naphtha and light cycle oil fractions when said FCC process is conducted without said regenerable sorbent under substantially identical FCC reaction conditions.

101. The process of Claim 98 wherein said cracked hydrocarbon product recovered in said recovering step comprises FCC naphtha having a sulfur content at

least about 75 wt.% less than the sulfur content of said FCC naphtha when said FCC process is conducted without said regenerable sorbent under substantially identical FCC reaction conditions.

102. The process of Claim 98 wherein said cracked hydrocarbon product recovered in said recovering step comprises FCC naphtha having a sulfur content at least about 90 wt.% less than the sulfur content of said FCC naphtha when said FCC process is conducted without said regenerable sorbent under substantially identical FCC reaction conditions

103. The process of Claim 98 wherein said cracked hydrocarbon product recovered in said recovering step has a sulfur content at least about 50 wt.% less than the sulfur content of said cracked hydrocarbon product when said FCC process is conducted without said regenerable sorbent under substantially identical FCC reaction conditions.

104. The process of Claim 98 wherein said cracked hydrocarbon product recovered in said recovering step comprises FCC naphtha and light cycle oil fractions having a sulfur content at least about 75 wt.% less than the sulfur content of said FCC naphtha and light cycle oil fractions when said FCC process is conducted without said regenerable sorbent under substantially identical FCC reaction conditions.

105. The process of Claim 98 wherein said cracked hydrocarbon product recovered in said recovering step comprises FCC naphtha and light cycle oil fractions having a sulfur content at least about 90 wt.% less than the sulfur content of said FCC naphtha and light cycle oil fractions when said FCC process is conducted without said regenerable sorbent under substantially identical FCC reaction conditions.

106. The process of Claim 98 wherein regenerable sorbent is present in said reaction zone an amount of from about 1 to about 10 wt%, based on the weight of the FCC catalyst present in said reaction zone.

107. The process of Claim 98, wherein said a refractory inorganic oxide cracking catalyst consists essentially of a metal-substituted refractory inorganic oxide cracking catalyst.

108. The process of Claim 107, wherein said the metal of said active metal oxide sulfur sorbent is the same metal as the metal of said metal-substituted refractory inorganic oxide cracking catalyst sorbent.

109. The process of Claim 108, wherein said metal-substituted refractory inorganic oxide cracking catalyst comprises zinc aluminate.

110. The process of Claim 107, wherein said metal-substituted refractory inorganic oxide cracking catalyst comprises zinc aluminate.

111. The process of Claim 98, wherein said active metal oxide sulfur sorbent comprises zinc oxide.

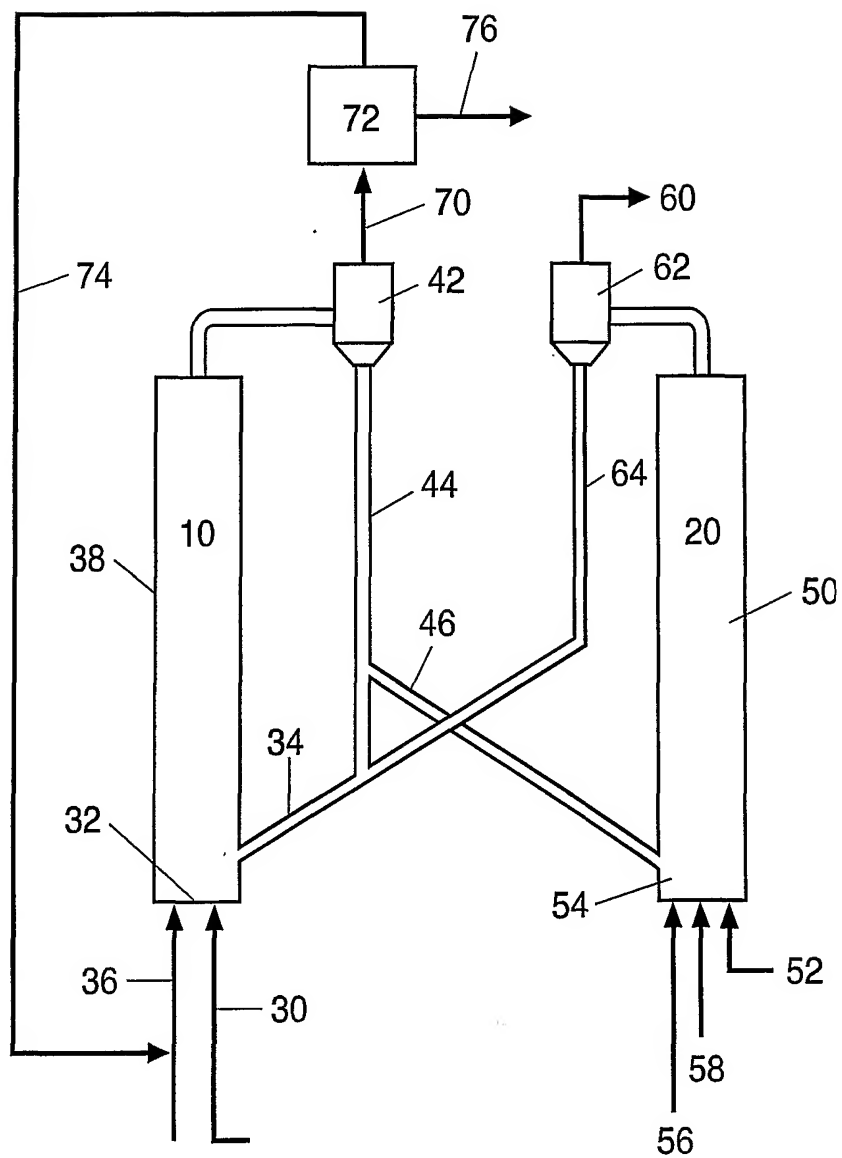
112. The process of Claim 98, wherein said active metal oxide sulfur sorbent comprises zinc titanate.

113. The process of Claim 107, wherein said metal-substituted refractory inorganic oxide cracking catalyst comprises iron aluminate.

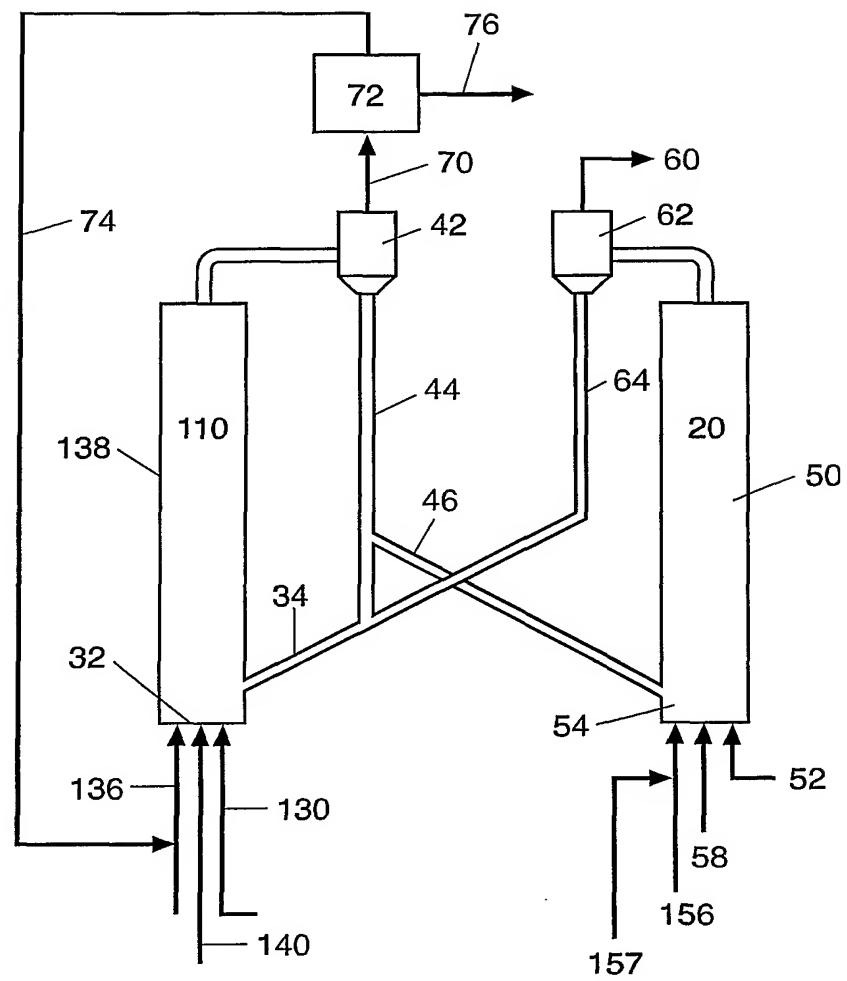
114. The process of Claim 108, wherein said metal-substituted refractory inorganic oxide cracking catalyst comprises iron aluminate.

115. The process of Claim 98, wherein said active metal oxide sulfur sorbent comprises an iron oxide.

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**Figure 1**

2/2

**Figure 2**

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/26019

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C10G 29/16, 25/00, 25/06, 25/12

US CL : 208/208R, 244, 247, 299

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 208/208R, 244, 247, 299

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
Please See Continuation Sheet

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 4,113,606 A (MULASKEY) 12 September 1978 (12.09.1978), column 1, line 42 through column 2, line 2; column 3, line 35 through column 4, line 15.	1,4-7,9-18,20-48,50-70,72-76,78-85,87-89,91-98,100-115 ----- 2,3,8,19,49,71,77,86,90,99
Y	US 5,776,331 A (KHARE et al) 07 July 1998 (07.07.1998), column 4, line 62 through column 5, line 18.	2,3,8,19,49,71,77,86,90,99
A	US 4,088,736 A (COURTY et al) 09 May 1978 (09.05.1978).	1-115
A	US 4,298,460 A (FUJIMORI et al) 03 November 1981 (03.11.1981).	1-115
A	US 5,045,522 A (KIDD) 03 September 1991 (03.09.1991).	1-115
A	US 5,059,302 A (WEINBERG et al) 22 October 1991 (22.10.1991).	1-115
A	US 5,254,516 A (GUPTA et al) 19 October 1993 (19.10.1993).	1-115



Further documents are listed in the continuation of Box C.



See patent family annex.

\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T"

later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X"

document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y"

document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&"

document member of the same patent family

Date of the actual completion of the international search

13 November 2001 (13.11.2001)

Date of mailing of the international search report

13 DEC 2001

Name and mailing address of the ISA/US

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**INTERNATIONAL SEARCH REPORT**

International application No.

PCT/US01/26019

**C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,914,288 A (TURK et al) 22 June 1999 (22.06.1999).	1-115
A	US 5,914,292 A (KHARE et al) 22 June 1999 (22.06.1999).	1-115
A	WO 99/42201 A1 (VIERHEILIG) 26 August 1999 (26.08.1999).	1-115



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/26019

### Continuation of B. FIELDS SEARCHED Item 3:

EAST search terms: desulfurization, hydrocarbon, oil, fuel, adsorbent, sorbent, zinc, iron, aluminate, oxide, cracking, catalyst  
STN ENCOMPAT search terms: adsorbent, zinc, iron, aluminum oxide, silica, zeolite, zinc oxide, iron oxide

**[54] CATALYTIC CRACKING OF PARAFFINIC  
FEEDSTOCKS WITH ZEOLITE BETA**

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[73] **Assignee:** Mobil Oil Corporation, New York, N.Y.

[21] **Appl. No.:** 352,640

[22] **Filed:** May 12, 1989

**Related U.S. Application Data**

[63] Continuation of Ser. No. 105,630, Oct. 7, 1987, abandoned, which is a continuation-in-part of Ser. No. 4,805, Jan. 12, 1987, abandoned, and a continuation-in-part of Ser. No. 825,171, Mar. 3, 1986, abandoned, and a continuation-in-part of Ser. No. 686,772, Dec. 27, 1984, abandoned.

[51] **Int. Cl.<sup>4</sup>** ..... C10G 11/05; C10G 57/00

[52] **U.S. Cl.** ..... 208/67; 208/49;  
208/120; 585/323; 585/739

[58] **Field of Search** ..... 208/120, 49, 67;  
585/739, 323, 446

**[56] References Cited****U.S. PATENT DOCUMENTS**

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3,308,069	3/1967	Wadlinger et al. ....	502/64
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**FOREIGN PATENT DOCUMENTS**

0094827 11/1983 European Pat. Off. .... 208/120

*Primary Examiner*—Anthony McFarlane

*Attorney, Agent, or Firm*—Alexander J. McKillop;

Charles J. Speciale; Malcolm D. Keen

**[57] ABSTRACT**

Heavy hydrocarbon oils of high paraffin content are catalytically cracked using zeolite beta. The paraffin content of the oil is at least 20 weight percent or higher. The gasoline cracking products have a high octane rating and the higher boiling products a decreased pour point resulting from the dewaxing activity of the zeolite beta. The use of cracking temperatures above 500° C., preferably above 550° C., also improves iso-butene production.

**13 Claims, No Drawings**

# CATALYTIC CRACKING OF PARAFFINIC FEEDSTOCKS WITH ZEOLITE BETA

## CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuation of Ser. No. 07/105,630, filed 10/7/87, now abandoned, which is a continuation-in-part of Ser. No. 07/004,805, filed 1/12/89, now abandoned, which is a continuation-in-part of Ser. No. 06/825,171, filed 3/3/86, now abandoned, which is a continuation-in-part of Ser. No. 06/686/772, filed 12/27/84, now abandoned. The contents of Ser. Nos. 07/004,085 and 06/686,772 are incorporated in the application by reference.

## FIELD OF THE INVENTION

This invention relates to a process for the catalytic cracking of heavy oil feeds using a cracking catalysts comprising zeolite beta. It relates more particularly to a process for the catalytic cracking of paraffinic feeds with a catalyst of this type.

## BACKGROUND OF THE INVENTION

The catalytic cracking of hydrocarbon oils using acidic cracking catalysts is a well established process which has, for a number of years, used a number of different types of catalytic cracking units including, in the early years, fixed bed crackers of the Houdrifiow type and later, moving bed units such as the Thermoform Catalytic Cracking (TCC) units and fluidized bed catalytic cracking units (FCC). Of these, fluid catalytic cracking (FCC) has now become the predominant type of unit for catalytic cracking. In both the moving, gravitating bed and moving, fluidized bed processes, the feedstock to the unit is brought into contact with a hot, continuously circulating, cracking catalyst to effect the desired cracking reactions, after which the cracking products are separated from the catalyst which is regenerated by oxidation of the coke which accumulates on the catalyst. Oxidative regeneration in this way serves the purpose both of removing the coke which deactivates the catalyst and also brings the catalyst back up to the temperature required to maintain the endothermic cracking reactions. The hot, regenerated catalyst is then recirculated to the reactor where it is again brought into contact with the feedstock. The moving bed (TCC) process, the catalyst is generally in the form of beads which move through the reactor and the regenerator in a solid, gravitating mass whereas in the FCC process, the catalyst is in the form of a fluent powder, typically of about 100 microns particle size.

The catalysts used in catalytic cracking, whatever the type of unit employed, possess acidic functionality in order to catalyze the cracking reactions which occur. Initially, the acidic functionality was provided by amorphous type catalysts such as alumina, silica-alumina or various acidic clays. A significant improvement in the process was provided by the introduction of crystalline, zeolitic cracking catalysts in the 1960's and this type of catalyst has now become universally employed. The zeolites which are used for this purpose can generally be characterized as large pore zeolites because it is essential that the internal pore structure of the zeolite which contains the bulk of the acidic sites on the zeolite should be accessible to the bulky, polycyclic aromatic materials which make up a large portion of the heavy oil feeds to the process. Large pore zeolites which have

been used for this purpose include mordenite and the synthetic faujasite zeolites X and Y. Of these, zeolite Y has now become the zeolite of choice because of its superior stability to hydrothermal degradation, particularly when it is used in the forms of a rare earth exchanged zeolite (REY) or the so-called ultrastable Y (USY).

Although most of the feeds to catalytic cracking units contain significant amounts of high boiling aromatic constituents, some feeds, particularly from Southeast Asian and Pacific sources contain relatively large amounts of waxy paraffins which are relatively refractory towards catalytic cracking, especially in the presence of aromatics. Feedstocks of this type are generally difficult to process in conventional catalytic cracking processes regardless of the type of catalyst used: when waxy gas oils derived from crudes of this type are passed through the unit, the gasoline product tends to have a relatively low octane number and the unconverted fraction in which the refractory paraffins tend to concentrate, has a very high pour point which makes it unsuitable for use as a blending component in fuel oils without the addition of cutter stock. Furthermore, recycle of the unconverted fraction is of limited utility because of the refractory nature of the paraffins in this material.

The problems presented by the presence of waxy components in petroleum oils have, of course, been known for a long time and various processes have been evolved for removing the waxy components from various distillate fractions including lubricating oils, middle distillates including heating oils and jet fuels and gas oils. Various catalytic hydro-dewaxing processes have been developed for this purpose and these processes have generally removed the longer chain n-paraffins and slightly branched chain paraffins by selectively cracking these materials to produce lower molecular weight products which may be removed by distillation. In order to obtain the desired selectivity, the catalyst has usually been an intermediate pore size zeolite with pore size which admits the straight chain n-paraffins either alone or with only slightly branched chain paraffins, but which excludes more highly branched materials, naphthenes and aromatics. Catalytic hydro-dewaxing processes of this kind are described, for example, in U.S. Pat. Nos. 3,668,113; 3,894,938; 4,176,050; 4,181,598; 4,222,855; 4,229,282; and 4,247,388. However, the intermediate pore size zeolites such as ZSM-5, which are highly effective as dewaxing catalysts in these hydrogenative processes using relative light feeds, are generally unsuitable for use as cracking catalysts because their pores are too small to admit the bulky, polycyclic aromatics into the internal pore structure of the zeolite where cracking can take place. They have not, therefore, been used as such for catalytic cracking although they have been combined with large pore zeolites in catalytic cracking catalysts in order to improve the octane rating of the naphtha cracking product, but even when combined with a conventional cracking catalyst in this way, they tend to produce too much dry gas and accordingly, they are unable to function effectively as cracking catalysts for waxy feeds. The problem of dealing with feeds of this kind has therefore persisted.

## SUMMARY OF THE INVENTION

It has now been found that zeolite beta is an extremely effective cracking catalyst for highly paraffinic feeds, being capable of producing gasoline of improved octane number, with greater potential alkylate yield, and with reductions in the pour point (ASTM D-97) of the higher boiling cracking product fractions. According to the present invention, therefore, a process for the catalytic cracking of a highly paraffinic hydrocarbon oil employs a cracking catalyst comprising zeolite beta.

The feed to the cracking process may be subjected to hydrotreating in order to improve its crackability by saturating any aromatic ring structures which may be present together with ring opening of aromatics and naphthenes, according to the extent of the treatment. Initial treatment of the feed in this way permits feeds of lower paraffin content to be employed and therefore permits a greater number of feed types to be cracked to the greatest advantage. By employing severe hydrotreating, relatively aromatic feeds can be treated to increase their paraffin content to levels where the benefits of the present process become apparent.

It has also been found that the use of relatively high cracking temperatures, typically greater than about 500° C. (about 930° F.) and preferably above about 550° C. (about 1020° F.), the proportion of isobutene in the cracking products is significantly increased. This finding is of particular utility when octane-improving additives such as methyl tertiary butyl ether (MTBE) are to be produced because iso-butene is a key starting material in their production.

## DETAILED DESCRIPTION

## General Considerations

The present catalytic cracking process is applicable to the catalytic cracking of highly paraffinic feeds, that is, to feeds which comprise at least 20% by weight paraffins. The process may be carried out in any of the conventional type of catalytic cracking units, implying that it will normally be carried out in a moving, gravitating bed (TCC) unit or a fluidized bed (FCC) catalytic cracking unit in the absence of added hydrogen. Because both the FCC and TCC processes are well established, it is not necessary to describe their individual features in detail, except to point out that both are endothermic catalytic cracking processes which are operated at elevated temperatures, typically in excess of about 550° C. (about 1020° F.) usually under slight superatmospheric pressure in the reactor. The catalyst passes continuously in a closed loop from the cracking reactor to the regenerator in which the coke which accumulates on the catalyst is removed oxidatively, both in order to restore activity to the catalyst and to supply heat for the endothermic cracking requirements. The oxidative regeneration is carried out in a bed of the same general type as the reactor bed so that in a TCC process, regeneration is carried out in a moving, gravitating bed in which the catalyst particles move downwards countercurrent to the flow of regeneration gas and in the various FCC processes, regeneration is carried out in a fluidized bed, typically using a dense phase bed or a combination of dense phase bed with a dilute phase transport bed, according to the unit. Typical FCC processes are disclosed in U.S. Pat. Nos. 4,309,279; 4,309,280; 3,849,291; 3,351,548; 3,271,418; 3,140,249; 3,140,251; 3,410,252; 3,140,253; 2,906,703; 2,902,432; regeneration techniques applicable to FCC are dis-

closed, for example, in U.S. Pat. Nos. 3,898,050, 3,893,812 and 3,843,330 to which reference is made for a description of particular details of such processes.

In general, the present catalytic cracking process will be carried out under conditions comparable to those used in existing processes, having regard to the capabilities of the cracking unit, the exact composition of the feed and the type and distribution of the products which are desired. As is well known, some feeds are more refractory than others and require the use of higher temperatures and changes in the distribution of the products, for example, depending upon whether the production of naphtha or of distillate is to be maximized, will require other changes. Other changes in operating conditions may be required according to the catalyst circulation rate—a factor which is characteristic of the unit—and catalyst makeup rate. The extent to which changes in these operating conditions will affect the products obtained in any given unit will be known for that unit.

## Feedstocks

Feedstocks which are used in the present process are highly paraffinic petroleum fractions, that is, petroleum fractions which contain at least 20% by weight of waxy components. The waxy components will comprise normal paraffins and slightly branched chain paraffins with only minor degrees of short-chain branching, e.g. mono-methyl paraffins. In some cases, the petroleum fraction will contain at least 40% or even at least 60 wt. % of waxy components and indeed, the ability of the present catalysts to handle very highly paraffinic feeds enable certain refinery streams which are almost exclusively paraffinic, such as slack wax, to be cracked effectively to produce products of higher value. The presence of waxy components implies, of course, that the petroleum fraction has an initial boiling point which places the molecular weights of the paraffins in a range where they will be waxy in nature. This normally means that the fraction will have an initial boiling point above that of the naphtha boiling range materials, e.g. above about 200° C. (about 390° F.) and more usually the initial boiling point will be above about 300° C. (about 570° F.). In most cases, the initial boiling point of the fraction will be at least 345° C. (about 650° F.). In most cases, the end point will not be higher than 565° C. (about 1050° F.) although higher end points may be encountered, depending upon the distillation units being used in advance of the cracker although they may include significant amounts of heavy ends which are essentially non-distillable. Generally, therefore, the feedstocks which are used in the present process will have a boiling range within the range of 345° to 565° C. (about 650° to 1050° F.) although other boiling ranges, e.g. 300°–500° C. may also be encountered. The feeds can therefore be generally characterized as gas oils, including vacuum gas oils although other highly paraffinic refinery streams such as slack wax may also be catalytically cracked using the present catalysts.

The feeds will usually contain varying amounts of aromatic compounds, generally polycyclic aromatics with alkyl side chains of varying lengths which will be removed during the cracking process. However, certain feeds may be so highly paraffinic that the content of aromatics will be quite small, for example, in the slack waxes mentioned above. Naphthenes will also generally be present in varying amounts, depending upon the nature of the feed and its processing prior to the cata-

lytic cracking step. In general, the feedstocks will not contain unusually large amounts of aromatics.

The feed may be subjected to various treatments prior to cracking, either to improve the cracking operation by providing a feed of improved crackability or to improve the distribution of the products or their properties. Hydrotreating of the feed is a particularly useful adjunct because it removes heteroatom-containing impurities and saturates aromatics; in doing so, it reduces catalyst poisoning by the heteroatom contaminants, especially nitrogen and sulfur, reduces the SO<sub>x</sub> emissions from the unit and, in increasing the hydrogen content of the feed to a level which approaches that of the products, improved product distribution and feed crackability. Severe hydrotreating to reduce aromatic unsaturation by hydrogenation and ring opening is a particularly useful technique since it enables the advantages of the present process to be achieved with feeds which are initially less paraffinic. Conventional hydrotreating catalysts and conditions may be used, with higher hydrogen pressures preferred with feeds of higher aromaticities in order to increase aromatics saturation.

The compositions of two typical, waxy gas oil feeds are set out in Tables 1 and 2 below; of two hydrotreated feeds in Tables 3 and 4 and of four slack wax feeds in Table 5. These feeds, either on their own or with other feeds may be used in the present process.

TABLE 1

Minas Gas Oil	
Nominal boiling range, °C. (°F.)	345°-540° (650°-1000°)
API Gravity	33.0
Hydrogen, wt %	13.6
Sulfur, wt %	0.07
Nitrogen, ppmw	320
Basic Nitrogen, ppmw	160
CCR	0.04
Composition, wt %	
Paraffins	60
Naphthenes	23
Aromatics	17
Bromine No.	0.8
KV, 100° C., cSt	4.18
Pour Point, °C. (°F.)	46 (115)
95% TBP, °C. (°F.)	510 (950)

TABLE 2

Gippsland Gas Oil		
API Gravity	33.8	
Pour Point, °C. (°F.)	40 (105)	
KV at 100° C., cSt	3.0	
Aniline Point, °C. (°F.)	95 (202.5)	
Bromine Number	1.7	
Refractive Index at 70° C.	1.4538	
Hydrogen, wt %	13.67	
Sulfur, wt %	0.15	
Nitrogen, ppm	180	
Nickel, ppm	0.14	
Vanadium, ppm	0.10	
Iron, ppm	2.0	
Copper, ppm	*0.1	
Conradson Carbon, wt %	0.13	
Molecular Weight, av.	313	
Composition, wt %		
Paraffins	62.9	
Mononaphthenes	1.6	
Polynaphthenes	10.7	
Aromatics	24.7	
Distillation (D-1160)	°C.	°F.
IBP	205	401
5%	280	537
10%	309	589
30%	367	693

TABLE 2-continued

50%	396	745
70%	420	789
90%	457	855
95%	474	886
EP%	485	905

\*Less Than

TABLE 3

HDT Minas Feed	
Nominal boiling range, °C. (°F.)	345°-540° (650°-1000°)
API Gravity	38.2
H, wt. pct.	14.65
S, wt. pct.	0.02
N, ppmw	16
Pour Point, °C. (°F.)	38 (100)
KV at 100° C., cSt	3.324

TABLE 4

HDT Statfjord Feed	
Nominal boiling range, °C. (°F.)	345°-455° (650°-850°)
API Gravity	31.0
H, wt. pct.	13.76
S, wt. pct.	0.012
N, ppmw	34
Pour Point, °C. (°F.)	32 (90)
KV at 100° C., cSt	4.139
Composition, wt %	
Paraffins	30
Naphthenes	42
Aromatics	28

TABLE 5

Slack Wax Composition - Arab Light Crude				
Composition, wt %	A	B	C	D
Paraffins	94.2	81.8	70.5	51.4
Mono-naphthenes	2.6	11.0	6.3	16.5
Poly-naphthenes	2.2	3.2	7.9	9.9
Aromatics	1.0	4.0	15.3	22.2

### Cracking Catalyst

The cracking catalyst used in the present process comprises zeolite beta as its essential cracking component. Zeolite beta is a known zeolite which is described in U.S. Pat. Nos. 3,308,069 and RE 28,341, to which reference is made for a description of this zeolite, its method of preparation and its properties.

Zeolite beta may be synthesized with relatively high silica:alumina ratios, for example, in excess of 100:1 and it is possible to achieve even higher ratios by thermal treatments including steaming and acid extraction, and in this was it is possible to make highly siliceous forms of the zeolite with silica:alumina ratios ranging from the lowest ratio at which the zeolite may be synthesized up to 100:1, 1,000:1, 30,000:1 or even higher. Although these forms of the zeolite would be capable of being used in the present process, the fact that catalytic cracking requires the catalyst to possess a relatively high degree of acidity, generally implies that the more acidic materials, with silica:alumina ratios from about 15:1 to 150:1 will be preferred with ratios from 30:1 to about 70:1 giving very good results. Because zeolite beta may be synthesized relatively easily with silica:alumina ratios of this magnitude, the zeolite may generally be used in its as-synthesized form, following calcination to remove the organic cations used in its preparation. For similar reasons, it is generally preferred not to incorporate substantial amounts of alkali or alkaline earth metal

cations into the zeolite, as disclosed in U.S. Pat. No. 4,411,770, because these will generally decrease the acidity of the material. If lower acidity should be desired, however, it is normally preferred to secure it by using zeolite forms of higher silica:alumina ratio rather than by adding alkali or alkaline earth metal cations to counter the acidity, because the more highly siliceous forms of the zeolite tend to be more resistant by hydrothermal degradation. Acid extraction is a preferred method of dealuminization either on its own or with preliminary steaming; dealuminized catalysts made in this way have been found to have improved distillate (G/D) selectivity.

The acidic functionality of the zeolite at the time that it is used as fresh catalyst in the process, is typically in excess of about 0.1, as measured by the alpha activity test, with preferred alpha activities being in the range of from 1 to 500 or even higher, and more commonly in the range of 5 to 100. The method of determining alpha is described in U.S. Pat. No. 4,016,218 and in *J. Catalysis*, VI, 278-287 (1966), to which reference is made for a description of the method. However, it should be remembered that the initial alpha value will be relatively rapidly degraded in a commercial catalytic cracking unit because the catalyst passes repeatedly through steam stripping legs to remove occluded hydrocarbons and in the regeneration process, a considerable amount of water vapor is released by the combustion of the hydrocarbonaceous coke which is deposited on the zeolite. Under these conditions, aluminum tends to be removed from the framework of the zeolite, decreasing its inherent acidic functionality.

Zeolite beta may be synthesized with trivalent framework atoms other than aluminum to form, for example, borosilicates, borosilicates, gallosilicates or galloaluminosilicate structural isotypes. These structural isotypes are considered to constitute forms of zeolite beta, the term zeolite beta being used to refer to materials of ordered crystalline structure possessing the characteristic X-ray diffraction of zeolite beta. The zeolite may be partially exchanged with certain cations in order to improve hydrothermal stability, including rare earths and Group 1B metals such as samarium, lanthanum, cerium, neodymium, praseodymium, silver or copper.

The zeolite beta is capable of catalyzing the desired cracking reactions on its own but in order to resist the crushing forces and attrition which are encountered in a commercial catalytic cracking unit, it will generally be formulated with a matrix or binder in order to improve its crushing strength and attrition resistance. The zeolite will therefore generally be incorporated in a clay or other matrix material such as silica, alumina, silica/alumina or other conventional binders. The binder material imparts physical strength to the catalyst particle and also enables the density of the catalyst particles to be regulated for consistent fluidization in FCC units. Generally, the amount of zeolite in the catalyst particles will be in the range of 5 to 95 wt. percent, with amounts from 10 to 60 wt. percent being preferred.

The binder may, and usually does, have some significant catalytic activity of its own but it will generally be preferred that the total acidic functionality provided by the binder will be only a minor amount of the total catalyst activity, as determined by the alpha test, because it is the zeolite which provides the particular, selective cracking characteristics which are desired with the paraffinic feeds.

Because catalytic cracking, which is generally carried out in the absence of added hydrogen, does not require the presence of a hydrogenation-dehydrogenation component as does hydrocracking, there is no need for any such component in the present cracking catalysts. Nevertheless, metal components may be present for other purposes, notably to promote the oxidation of carbon monoxide to carbon dioxide in the regenerator, as described in U.S. Pat. Nos. 4,473,658; 4,350,614; 4,174,272; 4,159,239; 4,093,568; 4,072,600; 4,541,921; 4,435,282; 4,341,660 and 4,341,623 to which references is made for a description of the use of oxidation promoters for this purpose. Typical oxidation promoters are the noble metals, especially platinum, and generally they will be present, if at all, in amounts which do not exceed 1,000 ppmw, preferably not more than 500 ppmw with about 100 ppmw being a typical maximum. In certain cases, extremely small amounts of promoter down to 0.1 ppmw may be sufficient and amounts of 0.1-100 ppmw are by no means uncommon. The oxidation promoter may be present on the catalyst or as a separate component.

Other zeolites in addition to the zeolite beta may be present in the catalyst and generally these will be other conventional cracking catalysts such as zeolite Y or intermediate pore size zeolites such as ZSM-5 which may be present to obtain further improvements in the octane number of the naphtha cracking products. Generally, if other zeolites are present in the catalyst for the purpose of octane improvement, they will be used in amounts less than that of the zeolite beta, for example, usually less than 50 wt. percent of the amount of the zeolite beta and typically from 10 to about 30 percent by weight of the zeolite beta, as described, for example, in U.S. Pat. Nos. 3,769,202, 3,758,403, 3,894,931, 3,894,933, and 3,894,934, although even smaller amounts, for example, 0.1 to 0.5 wt. percent may be used, as described in U.S. Pat. No. 4,309,279, to which reference is made for a description of the use of intermediate pore zeolites in cracking catalysts for this purpose. Copending application Ser. No. 775,189, filed 12 September 1985, discloses a process for catalytic cracking with mixtures of faujasite-type zeolites and zeolite beta.

When the catalyst is to be used in a moving bed process, it will usually be formed into pills, extrudates or oil-dropped spheres with an equivalent particle diameter of 1/32 to 1/2 inch, preferably about 1/8 inch (about 1 to 6 millimeters, preferably about 2 millimeters). When the catalyst is intended for use in a fluid catalytic cracking process, it will usually be used in the form of a fine powder, typically of 10 to 300 microns particle size, typically about 100 microns.

#### Process Conditions

As mentioned above, the catalytic cracking process is an endothermic process which is carried out under high temperatures, with the heat required for the process supplied by the oxidation of the carbon (coke) which accumulates on the catalyst during the cracking part of the cycle. Thus, the process as a whole, including the regeneration, is operated in a heat-balanced mode, with the regenerated catalyst serving as the medium for transferring the heat produced in the regenerator to the endothermic cracking process. Each cracking unit will have its own particular operating characteristics, as noted above, and these will determine the exact conditions used in the unit. Generally, however, the conditions will be characterized as being of elevated temperature, typically in excess of about 550° C. (about 1020°

F.) and frequently even higher, although temperatures above about 760° C. (about 1400° F.) are infrequently encountered because they tend to cause sintering of the catalyst and are close to the metallurgical limits on most units. In riser type crackers, the quoted temperatures will be those prevailing at the top of the riser. Pressures, as noted above, are usually only slightly above atmospheric typically up to about 1000 kPa (abs.) (about 130 psig), more commonly up to about 500 kPa (abs.) (about 58 psig). Catalyst/oil ratios will generally be in the range 0.1–10, more commonly 0.2–5 (by weight, catalyst:oil).

Conversion, that is, the proportion of the feed converted to lower boiling products, is a significant process parameter and generally will be at least 50 percent by weight. So, in a 345° C. + (about 650° F.+) gas oil, at least 50 percent by weight of the feed will be converted to fractions boiling below 345° C. (about 650° F.). Usually, conversion will be in the range 50–80 percent or even higher, up to 90 weight percent. It may, however, be necessary to limit conversion because of downstream limitations, especially distillation capacity. One characteristic of the present process using highly paraffinic feedstocks with the zeolite beta cracking catalyst is that large quantities of light olefins are produced and although these are desirable because they can be converted to high octane naphtha in conventional alkylation units, the fractionators connected to the cracking unit may not be large enough to handle these quantities of light olefins.

If the cracking feed is contacted with the catalyst at relatively high temperatures, usually over about 500° C. (about 930° F.) and preferably above about 550° C. (about 1020° F.), the cracking products contain increased proportions of iso-butene, a key ingredient for the production of branched chain ether octane improvers such as MTBE as well as an alkylation feed. This represents a significant improvement since the yield of iso-butene from catalytic cracking operations is usually quite low.

#### Process Characteristics

In use, zeolite beta has shown itself to be a stable cracking catalyst which, especially in its dealuminized forms with higher silica:alumina ratios, has good hydrothermal stability and in this respect has good potential for use in commercial cracking units in which the catalyst circulates through steam stripping zones and is subjected to water vapor at high temperature during the regeneration. In addition, zeolite beta is notable for its ability to crack paraffins in preference to aromatics and it is the n-paraffins which are cracked in preference to iso-paraffins. Zeolite Y, by contrast, is more selective towards naphthenes and aromatics so that highly paraffinic stocks have been considered refractory towards cracking with this zeolite. Zeolite beta is well able to convert these materials to lower boiling products but if significant quantities of aromatics are present with a correspondingly lower paraffin content, the use of a mixed catalyst comprising zeolite beta and a faujasite type zeolite may be desirable, as described in co-pending application Ser. No. 775,189, to which reference is made for a description of a process using combination cracking catalysis of this type.

By preferentially cracking the waxy paraffins in the feed, zeolite beta effectively dewaxes the feed, so producing a lowering of the pour point in the unconverted fraction, e.g. the 345° C. + (about 650° F.+) fraction. The present cracking process may therefore be em-

ployed for non-hydrogenative gas oil dewaxing in circumstances where an aromatic product is acceptable. At higher conversion levels, typically greater than 60 or 70 weight percent, further lowering of the pour point in the unconverted fraction may be noted, indicating a preference for conversion of the higher molecular weight components. Although zeolite beta has a distillate selectivity comparable to that of dealuminized zeolite Y at comparable silica:alumina ratios, it has been found that as the paraffin content of the feed increases, zeolite beta becomes progressively more effective in removal of the waxy paraffinic components, as indicated by the pour point of the unconverted fraction.

The dewaxing of the unconverted fraction enables the end point of distillate fractions which are pour point limited to be extended. For example, it is possible to extend the light fuel oil (LFO) fraction into the 345° C. + (about 650° F.+) range because of the dewaxing effect of the catalyst, thereby enlarging the size of the LFO pool. Similarly, the pour point reduction of the 345° C. + (650° F.+) fraction may permit the end point of heavy fractions, e.g. heavy fuel oil (HFO) to be extended.

Another particular advantage of zeolite beta is that it produces an improvement in the octane rating of the gasoline boiling range product (approx. C<sub>5</sub>–165° C., C<sub>5</sub>–330° F.). Improvements of at least 2 and typically of 3 to 5 octane numbers (R+O) may be noted with cracking of highly paraffinic feeds over zeolite beta, as compared to cracking over conventional cracking catalysts based on zeolite Y. Octane ratings in excess of 90 (R+O) may be achieved. Furthermore, when the octane contribution from the alkylate fraction is considered, the improvement is even more marked: zeolite beta produces larger quantities of alkylate with a higher C<sub>4</sub>/C<sub>3</sub> olefin ratio than zeolite Y and the yield of gasoline plus alkylate is accordingly higher for zeolite beta than for zeolite Y. These characteristics make for a higher alkylate yield and alkylate quality for a further improvement in gasoline quality. Octane quality of the naphtha and of the alkylate is relatively constant with conversion although slight increases do occur at higher conversion levels, as is customary. Finally, the coke yield with zeolite beta is lower than with zeolite Y at comparable conversion levels.

#### EXAMPLES 1–4

These Examples compare the performance of two different cracking catalysts on two different feeds. One catalyst was a conventional catalyst based on zeolite Y and the other is based on zeolite beta.

The conventional catalyst was a sample of equilibrium Durabead 9A (trademark), a moving bed catalytic cracking catalyst removed from an operating refinery. It consisted of a conventional 12 wt. percent REY zeolite in a silica/alumina binder in bead form.

The zeolite beta catalyst consisted of 50 wt. percent zeolite beta (zeolite/silica/alumina ratio of 40:1, alpha activity of 400 in the hydrogen form) and 50 wt. percent alumina binder mixed together and extruded. The catalyst was dried and calcined for 3 hours at 540° C. (1000° F.) in nitrogen followed by 3 hrs. at 540° C. (1000° F.) in air. The sodium content of the catalyst was 495 ppm. The zeolite beta catalyst was then steamed at 700° C. (1290° F.) for 4 hrs., in 100% steam at atmospheric pressure to an alpha activity of 6.



The two catalysts were then tested for the catalytic cracking of two different gas oil feeds, whose properties are shown in Table 6 below.

TABLE 6

	Gas Oil Properties	
	Gas Oil A	Gas Oil B
API Gravity	23.7	32.9
Pour Point, °C. °F.	35 (95)	40 (105)
Aniline Point, °F.	71 (160)	94 (202)
Sulfur, wt %	0.51	0.15
Nitrogen, ppmw	1600	200
Nickel, ppmw	0.53	0.14
Vanadium, ppmw	0.24	0.10
Molecular Weight, av.	357	320
Paraffins, wt. %	16.4	62.2
Naphthenes, wt. %	37.8	13.6
Aromatics, wt. %	45.8	24.2

As is apparent, Gas Oil B is considerably more paraffinic than Gas Oil A.

The catalysts were each placed in a laboratory sized, fixed-bed cracking unit which simulates moving bed cracking and used to crack the two gas oil feeds. The conditions used and the results obtained are given in Tables 7 and 8 below.

TABLE 7

Example	Cracking Aromatic Gas Oil (Gas Oil A)	
	1	2
Catalyst	Zeolite Beta	Zeolite Y
Temperature °C. (°F.)	496 (925)	496 (925)
Cat/Oil (g. zeolite/g. oil)	0.38	0.36
Run Time (minutes)	10	10
Conversion, (vol %)	53	53
C <sub>5</sub> + Gasoline (vol %)	41.6	44.7
Total C <sub>4</sub> 's (vol %)	8.8	6.5
Dry Gas (wt %)	5.4	4.6
Coke (wt %)	3.4	3.6
Octane (R + O)	91.7	91.1
C <sub>3</sub> = (vol %)	4.7	2.6
C <sub>4</sub> = (vol %)	5.2	2.5
iso-C <sub>4</sub> (vol %)	2.9	3.1
Alkylate (vol %)	16.6	8.5
Alkylate (R + O)	94.1	93.6
Gasoline + Alky (vol %)	58.2	53.2
Gasoline + Alky Octane (R + O)	92.4	91.5

TABLE 8

Example	Cracking Paraffinic Gas Oil - Gas Oil B	
	3	4
Catalyst	Zeolite Beta	Zeolite Y
Temperature °C. (°F.)	496 (925)	496 (925)
Cat/Oil (g. zeolite/g. oil)	0.37	0.49
Run Time (minutes)	5	5
Conversion, (vol %)	60	60
C <sub>5</sub> + Gasoline (vol %)	42.2	45.5
Total C <sub>4</sub> 's (vol %)	17.0	13.0
Dry Gas (wt %)	7.6	6.5
Coke (wt %)	2.0	2.5
Octane (R + O)	90.2	86.0
C <sub>3</sub> = (vol %)	8.2	5.3
C <sub>4</sub> = (vol %)	11.1	5.3
iso-C <sub>4</sub> (vol %)	4.8	6.2
Alkylate (vol %)	32.8	18.5
Alkylate (R + O)	94.1	93.9
Gasoline + Alky (vol %)	75.0	64.0
Gasoline + Alky Octane (R + O)	91.9	88.3
LFO, vol % 215°-345° C. (420°-650° F.)	23.3	22.5
HFO, vol % 345° C. + (650° F. +)	16.7	17.5
LFO pour pt., °C. (°F.)	-4 (25)	2 (35)
HFO pour pt., °C. (°F.)	35 (95)	46 (115)

As shown in Tables 7 and 8, zeolite beta provides only marginal benefits over the conventional zeolite Y

cracking catalyst when relatively non-paraffinic feeds such as Gas Oil A are used. Although the octane number of the gasoline produced is about the same, the zeolite beta cracking produces a 0.9 higher gasoline and alkylate octane number and 5 vol. percent higher gasoline and alkylate. These benefits increase substantially when the feed is highly paraffinic. As shown in Table 8, zeolite beta cracking of the paraffinic Gas Oil B results in the production of significantly more gasoline plus alkylate (75.0 vol. percent, as compared to 64.0 vol. percent). Furthermore, the improved pour points of the heavier fractions are notable, as are the reduced coke yields and the higher yields of gasoline plus alkylate.

Somewhat surprisingly, the octane number of the gasoline and alkylate fraction produced by zeolite beta cracking is also significantly higher, a gasoline plus alkylate octane number (R + O) of 91.9 as compared to the 88.3 (R + O) of the gasoline and alkylate produced from zeolite Y catalytic cracking. Thus, the zeolite beta produced not only more gasoline, but gasoline with a higher octane number than the commercially used catalyst based on zeolite Y.

## EXAMPLES 4-13

In these Examples, two catalysts were tested on three different waxy gas oils of high paraffin content.

The first catalyst was a dealuminized zeolite Y catalyst prepared by the acid extraction of ultrastable zeolite Y (USY) using 1.0M HCl, followed by steaming at 650° C. (1200° F.) at atmospheric pressure in 100% steam for 24 hours. The final, steamed zeolite had a framework silica:alumina ratio of 226:1, as determined by temperature programmed ammonia desorption (TPAD).

The second catalyst was a calcined zeolite beta catalyst (30:1 silica:alumina) which had been subjected to the same steaming treatment (no acid extraction) to increase the framework silica:alumina ratio to about 228:1, as determined by TPAD. The TPAD analysis procedure used is described in the article by G. T. Kerr and A. W. Chester in *Thermochim. Acta*, 3, 113 (1971).

The catalysts were used for the fluidized bed cracking of the three gas oils described below, using a small scale, dense fluidized bed reactor operated in a cyclic mode to give 10 minutes cracking and 5 minutes helium purge followed by oxidative regeneration to completion (40% oxygen:60% nitrogen), with a final 1 minute helium purge. The catalyst was used in the form of the pure zeolite (50 cc) crushed to 60-80 mesh (U.S. Standard), mixed with 30 cc of acid-washed, calcined quartz chips (80-120 mesh, U.S. Standard, "Vycor"—trademark). Comparison runs to show the extent of thermal cracking were carried out with 80 cc of crushed "Vycor" chips. The reaction temperature in each case was 510° C. (950° F.) with space velocity (LHSV) varying from 1.5 to 12 hr<sup>-1</sup>. Product was accumulated over a series of 10 cycles; mass balances in all cases were greater than 95%. All products were analyzed by gas chromatograph.

The properties of the three heavy vacuum gas oils (HVGO) used in these experiments are given in Table 9 below.

TABLE 9

	Properties of Heavy Vacuum Gas Oils		
	HVGO-C	HVGO-D	HVGO-E
C (wt. %)	85.65	85.82	81.50



TABLE 9-continued

Properties of Heavy Vacuum Gas Oils			
	HVGO-C	HVGO-D	HVGO-E
H (wt. %)	12.13	12.67	13.28
O (wt. %)	0.30	—	—
N (wt. %)	0.09	0.0169	0.01
S (wt. %)	2.15	0.22	0.03
Ash (wt. %)	0.01	—	—
Ni (ppm)	0.5	*0.01	*1
V (ppm)	0.5	0.5	*1
CCR	0.44	—	—
Pour Point, °C. (°F.)	32 (90)	43 (110)	57 (135)
Distillation, wt. %			
215° C. - (420° F. -)	0	0	0
215°-345° C. (420-650° F.)	0	7.20	2.09
345°-455° C. (650-850° F.)	54.02	60.85	58.99
455°-580° C. (850-1075° F.)	34.73	28.33	36.26
580° C. + (1075° F. +)	11.25	3.62	2.66
P/N/A Composition, wt. %			
Paraffins	31	52	81
Aromatics	49	15	10
Naphthene	20	33	9

Note  
\*Less than

The results are given in Tables 10-12 below, the reported pour points being for the 345° C. + (650° F. +) fractions.

TABLE 10

FCC of HVGO-C				
Example	5	6	7	
Catalyst	Feed	De-Al Y	Beta (1)	Quartz
WHSV	10.2	9.9	4.5	
215° C. + Conv.	45.42	20.49	3.60	
345° C. + Conv.	72.86	36.08	13.13	
C1 + C2	1.54	0.74	1.10	
C3 + C4	7.58	3.10	.10	
C5-215° C.	36.33	16.65	1.53	
215°-345° C.	23.85	12.66	9.41	
345°-455° C.	54.02	18.83	41.84	57.90
455°-580° C.	34.73	5.64	16.98	22.20
580° C. +	11.25	2.67	5.10	6.80
Coke	3.56	2.93	0.99	
Dist. Selec.	32.70	35.10	71.70	
G/D	1.52	1.32	0.26	
Pour Pt, °C. (°F.) (2)	32 (90)	13 (55)	13 (55)	13 (55)

Note  
(1) Acid washed to 250:1 silica:alumina  
Pour point of 650° F. + fraction

TABLE 11

FCC of HVGO-D				
Example	8	9	10	
Catalyst	Feed	De-Al Y	Beta (1)	Quartz
WHSV	9.6	10.5	5.0	
215° C. + Conv.	65.02	29.92	1.23	
345° C. + Conv.	82.10	52.14	6.08	
C1 + C2	2.23	0.66	.13	
C3 + C4	17.46	8.97		
C5-215° C.	45.33	20.29	.16	
215°-345° C.	7.20	14.48	25.00	11.61
345°-455° C.	60.85	10.17	32.04	67.98
455°-580° C.	28.33	3.90	9.47	19.17
580° C. +	3.62	2.53	2.90	
Coke	3.89	0.67	0.94	
Dist. Selec.	9.55	36.80	72.50	
G/D	6.23	1.14	0.04	
Pour Pt, °C. (°F.)	43 (110)	33 (92)	27 (80)	43 (110)

TABLE 12

FCC of HVGO-E				
Example	11	12	13	
Catalyst	Feed	De-Al Y	Beta (1)	Quartz

TABLE 12-continued

FCC of HVGO-E			
Example	11	12	13
WHSV	13.0	10.2	5.0
215° C. + Conv.	69.00	69.15	2.34
345° C. + Conv.	77.30	78.17	4.08
C1 + C2	0.81	1.72	0.18
C3 + C4	11.45	25.45	
C5-215° C.	54.67	41.98	0.42
215°-345° C.	2.09	8.77	3.74
345°-455° C.	58.99	15.27	12.92
455°-580° C.	36.26	6.27	6.21
580° C. +	2.66	0.69	2.18
Coke	0.00	2.07	1.80
Dist. Selec.	8.82	7.30	41.40
G/D	8.18	7.51	0.25
Pour Pt, °C. (°F.)	57 (135)	54 (130)	18 (65)

\*Pour point of 650° F. + fraction

Comparison of Table 10-12 shows that the dewaxing ability of the zeolite beta is related to the paraffin content of the feed. For relatively less waxy HVGO-C (31% paraffins) there is no improvement in the pour point of the 345° C. + fraction, either by thermal cracking, cracking over the zeolite Y catalyst or over zeolite beta. As the paraffin content of the feeds increases in gas oils D and E (52 and 81% paraffins, respectively), so does the spread between the 345° C. + pour points for the products obtained with the zeolite Y and the zeolite beta catalysts. Although product distillate selectivities for the two zeolites are similar, the possibility of extending the distillate end point above 345° C. by reason of the reduced pour point permits an increase in distillate selectivity for the zeolite beta to be achieved.

## EXAMPLES 14-15

A steamed zeolite beta catalyst was used in these Examples with another waxy feed. The catalyst was prepared by the same method as in Examples 5-13 and used for cracking according to the same procedure as described there.

The properties of the waxy VGO feed used are shown in Table 13 below.

TABLE 13

VGO Feed	
API Gravity	33.4
Pour Point, °C. (°F.)	40 (105)
KV @ 40° C. cSt	9.55
KV @ 100° C., cSt	2.74
CCR	0.05
Aniline Pt, °C. (°F.)	92.5 (198.50)
C, wt %	86.10
H, wt %	13.76
S, wt %	0.13
N ppmw	140
Simulated Distillation: wt %	
215° C. -	1.46
215° C.-345° C.	29.40
345° C.-455° C.	61.71
455° C.-540° C.	7.43
540° C. +	0
P/N/A: wt %	
Paraffins	56.8
Naphthenes	14.8
Aromatics	29.4

The results of the cracking of the waxy VGO feed at two different severities are shown in Table 14 below, the pour point being of the 345° C. + (650° F. +) fractions.

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TABLE 14

FCC of Waxy VGO Feed		
Example	14	15
Catalyst	Beta	Beta
Temp, °C. (°F.)	445 (835)	505 (941)
Zeolite/Oil, wt	0.49	0.88
Catalyst/Oil, wt	0.49	0.88
345° C.-Conversion, wt %	54.1	79.5
Pour Pt. 215° C.+, °C. (°F.)	(70)	(50)
Pour Pt. 345° C.+, °C. (°F.)	29 (85)	18 (65)

These results show that the zeolite beta effectively dewaxes the high boiling function with increasingly lower pour point being obtained at higher conversions.

## EXAMPLES 16-19

Gas oil D was cracked in a fixed bed at 500° C. (925° F.) over an REY cracking (12% REY on silica-alumina) catalyst and a steamed zeolite beta cracking catalyst, prepared by the same method as in Examples 5-13. The LFO (230°-365° C., 450°-690° F.) distillate yield and cetane index were determined at two different conversion levels for each catalyst. The results are shown in Table 15 below.

TABLE 15

FCC of HVGO-D				
Example	Catalyst	345° C.+ Conversion	LFO Yield, vol. %	Cetane No.
16	REY	50.1	25.5	45.8
17	REY	57.6	21.1	41.4
18	Beta	52.3	21.3	43.1
19	Beta	55.5	22.3	42.3

The distillates from the beta catalyst are of similar cetane quality to those from REY.

## EXAMPLES 20-30

Cracking experiments were carried out with two different gas oils to demonstrate the effect of using high cracking temperatures. The compositions of the oils are shown in Table 16 below.

TABLE 16

Feedstock Properties		
Property	Paraffinic Gas Oil F	Paraffinic Gas Oil G
Hydrogen, wt pct.	13.76	13.28

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TABLE 16-continued

Feedstock Properties		
Property	Paraffinic Gas Oil F	Paraffinic Gas Oil G
Sulfur, wt pct.	0.13	0.03
Nitrogen, ppmw	140	100
Paraffins, wt pct.	56.80	81.00
Naphthenes, wt pct.	14.80	9.00
Aromatics, wt pct.	28.40	10.00
API Gravity	33.40	35.21
Pour Pt. °F.	+105	+135
TBP Boiling Range.		
5% @ °F.	455	—
50% @ °F.	717	—
95% @ °F.	920	—
Simulated Distillation, wt pct.		
IBP-420° F.	1.46	0.0
420-650° F.	29.40	2.1
650-850° F.	61.71	59.0
850-1075° F.	7.43	36.3
1075° F.+	0.0	2.7

The three gas oils identified above were subjected to catalytic cracking using three different catalysts whose identities are given in Table 17 below.

TABLE 17

Properties of Cracking Catalysts			
Catalyst Desig.	(A)	(B)	(E)
Zeolite Component	REY	Beta	Ultra-STABLE Y
wt. pct. Zeolite	12	100	100
wt. pct. Matrix	88	—	—
Zeolite alpha	8	12	5
Catalyst	TCC Equil	Steamed	Steamed
Pretreatment	Catalyst		
Steaming			
Severity			
Temp., °F.	TCC cond	1200	1200
Press, psia	TCC cond	29.4	29.4
% Steam	TCC cond	100	100
Duration	TCC cond	24	24

The results of cracking the highly paraffinic Gas Oil F with the two catalysts are given below in Table 18.

TABLE 18

Cracking Gas Oil F at 510° C.						
Example	20	21	22	23	24	25
Catalyst	Zeolite Beta	Zeolite Beta	Zeolite Beta	Ultra-Stable Y	Ultra-Stable Y	Ultra-Stable Y
Catalyst I.D.	(B)	(B)	(B)	(E)	(E)	(E)
Cat/Oil, g/g	0.88	0.94	2.86	0.89	1.25	1.79
Zeolite/Oil g/g	0.88	0.94	2.86	0.89	1.25	1.79
Conversion to C <sub>4</sub>	9.83	9.55	38.13	14.18	11.58	22.20
Yields, wt. pct.						
C <sub>1</sub> + C <sub>2</sub>	0.94	1.07	1.63	1.64	1.48	1.66
C <sub>3</sub> *	0.44	0.35	1.99	0.87	1.11	1.20
C <sub>3</sub> =	4.57	4.66	17.45	6.59	0.83	9.30
i-C <sub>4</sub>	0.69	0.33	4.47	1.55	3.26	3.00
n-C <sub>4</sub>	0.18	0.12	0.94	0.63	0.45	0.50
1-Butene	0.50	0.52	2.10	0.63	0.91	1.41
Isobutene	1.58	1.50	5.42	1.14	1.71	2.52
2-Butenes	0.93	1.00	4.13	1.13	1.83	2.61
Isobutene/C <sub>4</sub>	0.16	0.15	0.14	0.08	0.14	0.11
Isobutene/(C <sub>1</sub> + C <sub>2</sub> )	1.68	1.40	3.33	0.69	0.86	1.51
C <sub>3</sub> = i-C <sub>4</sub> + i-C <sub>4</sub> =, wt pct.	6.8	6.5	27.34	9.28	5.80	14.82

The results in Table 18 show that there is a significant increase in the proportion of isobutene produced with the zeolite beta cracking catalyst as compared to the USY catalyst.

Similar results were obtained with cracking Gas Oil F at 505° C. with the REY catalyst (A) and the zeolite beta catalyst (B) as reported in Table 19 below.

TABLE 19

Cracking Gas Oil F at 505° C.		
Example	26	27
Catalyst	REY in	Zeolite
SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	Beta	
Catalyst I.D.	(A)	(B)
Cat/Oil, g/g	7.50	1.05
Zeolite/Oil, g/g	0.87	1.05
Conversion to C <sub>4</sub> -	12.8	34.4
Yields, wt. pct.		
C <sub>1</sub> + C <sub>2</sub>	1.0	3.00
C <sub>3</sub> *	0.30	1.50
C <sub>3</sub> =	5.40	11.40
i-C <sub>4</sub>	1.40	4.00
n-C <sub>4</sub>	0.20	1.30
1-Butene	0.80	2.10
Isobutene	1.90	9.10
2-Butenes	1.80	2.00
Isobutene/C <sub>4</sub> -	0.15	0.26
Isobutene/(C <sub>1</sub> + C <sub>2</sub> )	1.90	3.03
C <sub>3</sub> = + i - C <sub>4</sub> +	8.7	24.5
i-C <sub>4</sub> =, wt. pct.		

At lower reaction severity (cat/oil ratio) the zeolite beta catalyst converts substantially more of the gas oil to the desired C<sub>4</sub>- products than the REY catalyst despite the comparable alpha values for the two catalysts.

Gas Oil G was also subjected to cracking at 510° C. using the zeolite beta and the USY catalysts with the results given in Table 20 below.

TABLE 20

Cracking Gas Oil G at 510° C.			
Example	28	29	30
Catalyst	Zeolite	Ultra-	Ultra-
	Beta	Stable Y	Stable Y
Catalyst I.D.	(B)	(E)	(E)
Cat/Oil, g/g	1.18	0.92	1.22
Zeolite/Oil, g/g	1.18	0.92	1.22
Conversion to C <sub>4</sub> -	27.17	12.26	27.90
Yields, wt. pct.			
C <sub>1</sub> + C <sub>2</sub>	0.77	0.77	1.71
C <sub>3</sub> *	1.12	0.71	1.86
C <sub>3</sub> =	12.85	5.82	13.39
i-C <sub>4</sub>	2.18	1.56	4.42
n-C <sub>4</sub>	0.54	0.26	0.72
1-Butene	1.57	0.66	1.26
Isobutene	4.75	1.27	2.84
2-Butenes	3.39	1.21	1.69
Isobutene/C <sub>4</sub> -	0.17	0.10	0.18
Isobutene/(C <sub>1</sub> + C <sub>2</sub> )	6.16	1.65	1.66
C <sub>3</sub> = + i - C <sub>4</sub> +	19.78	8.65	20.65
i-C <sub>4</sub> =, wt. pct.			

Again, there is a significant advantage for the zeolite beta catalyst in terms of the iso-butene production.

## EXAMPLES 31-32

The effect of process severity on the yields of isobutene and C<sub>4</sub>- was found by catalytically cracking Gas Oil F at 450° C. and 505° C. using the zeolite beta catalyst. The results are in Table 21 below.

TABLE 21

Effect of Process Severity on Cracking Gas Oil G		
Example	31	32
Catalyst	Zeolite	Zeolite
	Beta	Beta
Temperature, °C.	450	505
Catalyst I.D.	(B)	(B)

TABLE 21-continued

Effect of Process Severity on Cracking Gas Oil G		
Example	31	32
Cat/Oil, g/g	0.5	1.05
Zeolite/Oil, g/g	0.5	1.05
Conversion to C <sub>4</sub> -	13.3	32.8
Yields, wt. pct.		
C <sub>1</sub> + C <sub>2</sub>	1.50	3.00
C <sub>3</sub> *	0.60	1.50
C <sub>3</sub> =	3.80	11.40
i-C <sub>4</sub>	1.70	4.00
n-C <sub>4</sub>	0.40	1.10
1-Butene	0.70	2.10
Isobutene	3.00	9.10
2-Butenes	1.60	0.60
Isobutene/C <sub>4</sub> -	0.22	0.28
Isobutene/(C <sub>1</sub> + C <sub>2</sub> )	2.00	3.03
C <sub>3</sub> = i - C <sub>4</sub> +	8.5	24.5
i-C <sub>4</sub> =, wt. pct.		

These results show the desirability of using cracking temperatures above 500° C. for maximum iso-butene production; it is noted that isobutene selectivity increases with increasing temperature.

We claim:

1. A process for improving the gasoline yield and octane rating of the gasoline boiling range (C<sub>5</sub>-330° F.) product produced by the catalytic cracking of a highly paraffinic feedstock and alkylation of the iso-butene fraction produced in the cracking to produce an improved quantity of gasoline boiling range hydrocarbons comprising catalytically cracked gasoline and alkylate, which comprises:

- (i) contacting a feedstock having an initial boiling point above about 345° C. and comprising at least 40 weight percent paraffins with a circulating cracking catalyst comprising zeolite beta which includes no metal components in excess of 1000 ppmw at a temperature over 500° C. and in the absence of added hydrogen at a pressure of not more than 1000 kPa and a catalyst:oil ratio of 0.1:1-10:1 by weight to produce cracking products at conversion to lower boiling product of at least 50 weight percent, the cracking products including gasoline, butene and iso-butene;
- (ii) separating the cracking products;
- (iii) continuously regenerating the catalyst on a cyclic basis by oxidative removal of the carbon deposited on the cracking catalyst during the cracking;
- (iv) separating the cracking products to form a fraction containing an enhanced quantity of iso-butene, a gasoline boiling range fraction and a low pour point fraction boiling above the gasoline fraction;
- (v) producing alkylate from the iso-butene fraction to form an improved yield of a high octane rating alkylate fraction.

2. A process according to claim 1 in which the feedstock comprises at least 60 wt. % paraffinic components.

3. A process according to claim 1 in which the catalyst comprises 5 to 95 wt. % zeolite beta.

4. A process according to claim 1 in which the zeolite beta has a silica:alumina ratio of 15:1 to 150:1.

5. A process according to claim 1 in which the zeolite beta has an alpha activity of 1 to 500.

6. A process according to claim 1 in which the catalytic cracking process comprises a fluidized catalytic cracking process.

7. A process according to claim 1 in which the catalytic cracking process comprises a moving, gravitating bed catalytic cracking process.

8. A process according to claim 1 in which the zeolite beta comprises the sole zeolite cracking component in the catalyst.

9. A process according to claim 1 in which the oil is contacted with the catalyst at a temperature of at least 550° C.

10. A process according to claim 1 in which the cracking catalyst includes a carbon monoxide oxidation

promotor as a metal component in an amount from 0.1 to 1000 ppmw.

11. A process according to claim 10 in which the oxidation promotor is present in an amount of 0.1 to 100 ppmw.

12. A process according to claim 1 in which the conversion to lower boiling products is 50 to 90 weight percent.

13. A process according to claim 1 in which the octane rating of the gasoline and alkylate is at least 90 (R+O).

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# United States Patent [19]

Michlmayr

[11] 4,179,361

[45] Dec. 18, 1979

[54] **SORBENT REGENERATION IN A PROCESS  
FOR REMOVING SULFUR-CONTAINING  
IMPURITIES FROM MINERAL OILS**

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[21] Appl. No.: **960,501**

[22] Filed: **Nov. 13, 1978**

[51] Int. Cl.<sup>2</sup> ..... **C10G 29/16; C10G 25/12**

[52] U.S. Cl. .... **208/244; 208/246;  
252/411 S; 252/416**

[58] Field of Search ..... **208/244, 246; 252/416,  
252/420, 411 S**

[56]

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[57]

## ABSTRACT

Mineral oils containing minor or residual amounts of sulfur-containing impurities are upgraded by contact thereof with a cobalt oxide-supported sorbent under sulfur-sorbing conditions. The sorbent is regenerated by a set of sequential treatment steps.

**7 Claims, No Drawings**

# SORBENT REGENERATION IN A PROCESS FOR REMOVING SULFUR-CONTAINING IMPURITIES FROM MINERAL OILS

## BACKGROUND OF THE INVENTION

This invention relates to the separation of sulfur compounds from mineral oils, and more particularly to the use of a special sorbent and to its regeneration after use.

Generally, sulfur occurs in petroleum and syncrude stocks, tar sand oil, shale oil and the like, in such forms as organic mercaptans, sulfides, disulfides, and as a part of ring compounds such as thiophene, benzothiophene, and dibenzothiophenes and the like impurities. Usual practice in petroleum and syncrude refining is to remove at least the major portion of these impurities from the oil or from product fractions obtained from the oil, such as straight-run, gas oil, vacuum gas oil or the like fractions. Normally sulfur removal is by treatment using hydrogen and a catalyst under well-known hydrotreating, hydrofining and/or hydrodesulfurizing conditions. In general, the cost of sulfur removal by such treatments in terms of hydrogen consumed, light gas make, reduced catalyst life and the like costs, increases markedly with increasing degree of sulfur removal. When the mineral oil originally has but a minor content of sulfur or has been hydroprocessed to such a low sulfur content, for example in the range from 1 to 500 ppmw, catalytic hydroprocessing or further hydroprocessing may be uneconomical in terms of efficient usage of a costly catalyst. Consequently, there is a need for an effective means for removing a minor amount of sulfur-containing impurities from a mineral oil, especially of the residual impurities in a hydroprocessed oil. These impurities in general, or at least in large part, are of the thiophene type, for which relatively severe process conditions are usually required for their hydrogenative desulfurization.

It is an object herein to provide an effective regenerative sorbent process for removing residual and/or trace amounts of sulfur-containing impurities from a mineral oil.

## SUMMARY OF THE INVENTION

A non-hydrogenative process is provided for upgrading a mineral oil feed containing a minor amount of sulfur-containing impurities. In the process, a sulfur-containing sorbent and a resulting oil are produced by contacting the feed and a particulate sorbent, for example in a fixed-bed or fluid-bed mode, at a temperature in the range of from about 250° to 500° C. and a liquid hourly space velocity in the range of from about 0.1 to 20. The contacting is carried out in the substantial absence of water, that is, under oleaginous, in contrast to essentially aqueous as required for hydrolysis, conditions. The sorbent used consists essentially of a minor amount of cobalt oxide disposed upon porous alumina sized as particles normally employed for fixed-bed or fluid-bed usage. The oil resulting from the contacting has, relative to the feed, a substantially (at least 50%) lower content of the impurities. For convenience, and following custom, the content of impurities is expressed as sulfur in parts thereof per million parts of the total mixture, for example feed or resulting oil.

The afore-described sulfur-containing sorbent and resulting oil are separated, the latter for recovery and the former for continued use or ultimately, when its

capacity for sorbing sulfur has been reached, for regeneration in a sequence of steps or treatments, including:

(a) oxidizing at least a major portion of the sulfur content of said sulfur-containing sorbent by heating said sorbent in the presence of molecular oxygen at a temperature in the range of from about 200° to 800° C. for a period in the range of from about 0.5 to 2 hours;

(b) heating said oxidized sorbent resulting from step (a) at a temperature in the range of from about 700° to 1000° C. for a period in the range of from about 0.2 to 5 hours; and

(c) contacting the heated sorbent resulting from step (b) with wet air or steam at a temperature in the range of from about 400° to 600° C. for a period in the range of from about 0.5 to 2 hours.

In another aspect of the invention, sulfur-containing impurities in a hydrocarbon feed are removed in a two-stage sorption process. In the first stage, the feed contains more than 50 and less than about 500 ppmw of sulfur-containing impurities. This content of impurities is reduced to an amount in the range of from about 1 to 100, preferably 1 to 30, ppmw sulfur by contacting the feed with a copper-containing sorbent under known sorbing conditions for removing such impurities from a hydrocarbon mixture [e.g., using (1) copper chromite, metal or oxide, disposed upon an inert support as the sorbent, for example alumina, silica-alumina, magnesia, or the like; (2) a temperature in the range 0° to 400° C., and (3) with the feed in the liquid, gas, or both phases]. The resulting upgraded oil has a content of sulfur-containing impurities which is typically less than 50% of that of the feed and is usually in the range of from about 1 to 100 ppmw. It is then processed pursuant to the regenerative sorption process described above.

Other and preferred aspects of the invention and obvious variations thereof will be clear from the examples and description to follow.

## EMBODIMENT

In a preferred embodiment, sulfur-containing impurities are partially removed from a reformer fraction, for example a C<sub>7</sub>-C<sub>10</sub> fraction separated from a hydrofined gasoline-boiling-range straight-run refining product. The hydrofining is carried out under conventional hydrofining conditions, for example:

Temperature, °C.	250-500
Pressure, Atm. g.	10-120
Feed Rate, V/V/Hr	0.1-20
Hydrogen Rate, SCM/K1	50-2000

using a commercially available hydrocarbon hydrofining catalyst, for example cobalt-molybdenum disposed upon porous alumina. These conditions, of themselves, are of course not inventive. However, for present purposes and in their use, the severity of the conditions (usually temperature) are controlled so as to obtain a product having a residual sulfur impurities content of about 30-40 ppmw. Under conventional practices, the hydrofining process conditions are maintained such that the sulfur level of the product is about 1 ppmw. In terms of the plant size, requirements for a given throughput of feed, that for a 30-40 ppmw product sulfur level process is much smaller than that for the 1-ppmw-level product.

Because of savings in hydrofining plant size and of other advantages, including a more sulfur impurities-free final product, it is advantageous to remove the

aforementioned residual impurities in a two-stage regenerative sorption process, in neither of which stages hydrogen is added to the hydrocarbon feed, that is, a non-hydrogenative two-stage sorption process.

In the first stage of the sorption section of the process herein, the residual sulfur-containing impurities (30–40 ppmw) in the product from the above-described hydrofining stage) are substantially removed (e.g., to an amount in the 1–5 ppmw range) by contacting the product with a copper-containing regenerative sorbent under sulfur-impurity-sorbing conditions (for example, see U.S. Pat. No. 4,008,174 [–174] [R. L. Jacobson et al], which is incorporated herein by reference). The resulting low-sulfur product still contains residual sulfur of the thiophene type, which may be from 1–20 ppmw. While this content of sulfur is a hydrocarbon mixture may seem negligible, it is excessive where the mixture is to be reformed by contact thereof with a chlorided reforming catalyst of the platinum-rhenium-alumina type. Therefore, a second sorption stage is required in order to effectively reduce the content of thiophene-type impurities to a satisfactory level. Regeneration of the copper-containing sorbent is by any suitable conventional means, preferably in the manner described in the U.S. Pat. No. 4,008,174 cited above.

The low-sulfur product from the above-described sorption step is, for practical purposes, essentially fully desulfurized by contacting it with a sorbent having, in general, special affinity for thiophene-type impurities under suitable contacting conditions. The sorbent is a composite of cobalt oxide and porous alumina, the latter having a surface area in the 200–500-m<sup>2</sup>/g range and the former being about 10 weight percent thereof.

The contacting of the low-sulfur feed with the cobalt oxide-alumina composite is carried out using a bed or particulate sorbent in a fixed-bed reactor at a temperature of about 425° C., a liquid hourly space velocity, V/V/Hr, of about 0.2, and atmospheric pressure. Initially, the effluent product from the contacting contains no detectable sulfur. As the capacity of the sorbent for sulfur is approached, sulfur is detected and its use is discontinued. The sorbent is regenerated when a predetermined sulfur content is noticeable in the effluent product stream, for example 0.1 ppmw.

For the regeneration, the feeding of the hydrocarbon into the fixed-bed reactor is discontinued and, using an inert purge gas, for example nitrogen, residual hydrocarbons are swept from the reactor. In the first step of the regeneration, spent sorbent is then calcined in air by maintaining the bed at a temperature of about 315° C. while passing a stream of air through it. After a period of 0.5–1 hour, the sulfur content of the spent sorbent is substantially completely oxidized to sulfate and the composite comprises cobalt sulfate disposed upon porous alumina.

For the next step of the regeneration, the oxidized sorbent is maintained at a temperature of about 950° C. for a period of about 1 hour. During this period, sulfur oxide dissociation products are desirably removed from the reactor by passing a stream of nitrogen gas through the fixed bed. As an alternative, the dissociation products may be removed by maintaining the reactor at a subatmospheric pressure.

Next, the bed temperature is reduced to about 500° C., and while maintaining this temperature a stream of wet air (air saturated with water vapor at ambient conditions) is passed through the bed for a period of about one hour. The bed is now ready for further use in sorb-

ing thiophene-type impurities from the hydrocarbon feed.

#### The Feed

Distillable hydrocarbons (mineral oils) containing a minor amount of indigenous, residual and/or thiophene-type (thiophenes, substituted thiophenes and thiophene derivatives which are either indigenous to a mineral oil or present in such an oil as a result of processing thereof by known methods such as thermal cracking, hydrocracking, catalytic cracking, coking or the like) sulfur-containing impurities are satisfactory feeds for the process herein. In the case of the combination sorption process described above, the first stage of which employs a copper-containing sorbent, a satisfactory feed contains an amount of sulfur-containing impurities in the range of from about 50 to 500 ppmw. Although feeds containing more than 500 ppmw, for example as much as 1000 ppmw, may be used herein, such as usually more economically desulfurized by other known methods than by sorption by a copper-containing sorbent.

Representative mineral oils herein include, in general, distillates obtained from crude and syncrude oils as well as such oils after processing or partial processing having the aforementioned sulfur-impurities contents, such as gasoline, olefinic cracked gasolines, olefinic coker distillates, kerosene, light cycle oils, and jet fuel boiling-range hydrocarbons and fractions thereof. Other oils suitable for use herein include reformable hydrocarbon mixtures, aromatic hydrocarbon concentrates and the like particular distillable hydrocarbon fractions normally resulting from conventional hydrocarbon processing.

The process herein is especially useful and advantageous for upgrading hydrocarbon feeds which contain olefins. For example, a typical catalytically cracked gasoline (FCC gasoline) or coker distillate may contain 20–50% of olefins and have an octane number of about 90. Such a feed after sulfur removal by a typical hydroforming treatment usually has an octane number of about 65. In the present process, olefins, for practical purposes, are unaffected. The resulting product is, of course, an excellent octane-upgrading blending stock or gasoline.

#### The Sorbents

In the first stage of the two-stage sorbing mode of the invention, the copper-containing sorbent may be any material known and used in the art of sorbing sulfur-containing impurities from a mineral oil. Per se, these sorbents and their use in sorbing sulfur-containing impurities from an oil are not inventive. Copper disposed upon alumina is a preferred sorbent because it is available commercially and is conveniently regenerable.

In the second sorption stage, sorbents consist essentially of a minor amount of cobalt oxide disposed upon porous alumina. For effective removal of the impurities from the oil, a substantial cobalt-oxide surface must be presented for contact with the oil. Therefore, the alumina upon which the cobalt oxide is disposed must be porous and hence have at least a substantial pore volume, for example in the range of from about 0.3 to 1 and higher cc/gram. While any porous alumina is a satisfactory component of the sorbent, gamma-alumina is preferred. The sorbent may be prepared by any suitable known method, for example impregnation of commercially available alumina using a water-soluble cobalt salt which decomposes upon heating to cobalt oxide, for

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example cobalt nitrate and the like. The cobalt oxide-alumina sorbent may also contain minor amounts of other refractory oxides, such as magnesia, titania, calcium oxide and the like. Alumina undiluted by other refractory oxide carrier materials is preferred.

The amount of cobalt oxide desirably present in the sorbent may vary. In general, a satisfactory amount is in the range above 5 and below 50, preferably 5 to 30 weight percent.

#### Cobalt Oxide-Alumina Sorbing Conditions

The contacting in the sorbing of the impurities by the cobalt oxide-alumina sorbent is effected with the feed in the liquid and/or gas phase under conditions as follows:

	Broad Range	Preferred Range
Temperature, °C.	250-500	350-450
LHSV, V/V/Hr.	0.1-2.0	0.1-0.5

#### Spent Sorbent Regenerating Conditions

The oxidation of the spent or sulfur-containing sorbent is effected by contacting it with molecular oxygen, air, oxygen-enriched air, and the like gases under conditions as follows:

	Broad Range	Preferred Range
Temperature, °C.	700-1000	750-950
Time, Hours	0.5-2	0.5-1

The solid residue after dissociating the oxidized sorbent is heated while flowing a stream of wet air, steam or the like into contact therewith under conditions including:

	Broad Range	Preferred Range
Temperature, °C.	400-600	450-550
Gas Space Velocity, V/V/Hr	10-10,000	100-1000
Time, Hours	0.5-2	0.5-1
Pressure	0.5-2	Atmospheric

### EXAMPLES

The following examples further illustrate certain aspects of the invention.

#### EXAMPLE 1

A gasoline fraction containing 100 ppmw of thiophene sulfur was contacted with a sorbent which was a composite of porous alumina having disposed thereon, based upon alumina and calculated as metal, 10 weight percent of cobalt oxide. At 426° C. and a liquid hourly space velocity of 0.2, a 98% thiophene removal is accomplished for about 150 hours. Olefins in the feed are not affected. As the space velocity is increased, the thiophene removal is less effective, i.e., about 88% at LHSV=0.4 and about 60% at LHSV=1.0.

#### EXAMPLE 2

In a replicate of Example 1, the capacity of the sorbent was determined and found to be about 0.6 weight percent of thiophene sulfur. The spent sorbent was regenerated by steps including: (1) calcination thereof in air; (2) heating while maintaining subatmospheric

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pressure over the heated solid; and (3) passing wet air over the heated solid. This treatment, based upon fresh sorbent, was found to restore about 60% of the capacity which remains substantially constant after subsequent regenerations.

The above Examples 1 and 2 demonstrate that cobalt-alumina sorbents effectively remove thiophene-type impurities from a hydrocarbon feed.

#### EXAMPLE 3

The activity of a copper chromite-alumina sorbent for removing thiophene-type impurities from a gasoline was tested. For the test a light FCC naphtha was used. It had a total sulfur-containing hydrocarbon impurity content of 420 ppmw (as sulfur), of which a substantial portion was thiophene and thiophene-type impurities. The sorbent was a commercially available composite of copper chromite disposed upon porous alumina. Calculated as copper, it had a copper content of about 10 weight percent. The contacting was carried out at an LHSV of 0.2 and a temperature of 315° C. Only for a short period, about 40 hours, was sulfur removed to a low level; and even during this time, alkyl-substituted thiophenes were not removed. Further, in the case of thiophene, the removal was initially 100%, and then declined steadily, until after 40 hours it was only to the 30% level. Temperature and space velocity changes had virtually no effect upon the removal of thiophene-type impurities from the feed. Similar tests were made with similar results using copper in reduced form.

This example demonstrated that copper-alumina sorbents are not effective for the removal of thiophene-type impurities from a hydrocarbon feed, especially in terms of capacity.

What is claimed is:

1. A non-hydrogenative process for upgrading a mineral oil feed containing a minor amount of sulfur-containing impurities, comprising:

- (1) producing a sulfur-containing sorbent and a resulting oil by contacting said feed and a particulate sorbent at a temperature in the range of from about 250° C. to 500° C. and a liquid hourly space velocity in the range of from about 0.1 to 20, said sorbent consisting essentially of a minor amount of cobalt oxide disposed upon porous alumina, and said resulting oil, relative to the feed, having a substantially lower content of said impurities;
- (2) separating said resulting oil and sulfur-containing sorbent; and
- (3) regenerating said sorbent by steps including:
  - (a) oxidizing at least a major portion of the sulfur content of said sulfur-containing sorbent by heating said sorbent in the presence of molecular oxygen at a temperature in the range of from about 400° to 800° C. for a period in the range of from about 0.5 to 2 hours;
  - (b) heating said oxidized sorbent resulting from step (a) at a temperature in the range of from about 700° to 1000° C. for a period in the range of from about 0.2 to 5 hours; and
  - (c) contacting the heated sorbent resulting from step (b) with wet air or steam at a temperature in the range of from about 400° to 600° C. for a period in the range of from about 0.5 to 2 hours.

2. A process as in claim 1 wherein at least the major portion of said impurities are of the thiophene type and said amount thereof, calculated as sulfur in parts by



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weight per million parts of the feed, is in the range of from about 1 to 200 parts.

3. A process as in claim 2 wherein said feed, prior to said contacting with said sorbent, is contacted with a sorbent for sulfur-containing impurities selected from the group consisting of porous copper-containing sorbents, said contacting being under copper sulfur-sorbing conditions.

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4. A process as in claim 3 wherein said amount of thiophene-type impurities is in the range of from about 1 to 30 parts.

5. A process as in claim 1 wherein said heating of said oxidized sorbent in step (3a) is carried out under subatmospheric pressure.

6. A process as in claim 1 wherein during at least a portion of said heating in step (3a), a flowing carrier gas is passed into contact with said oxidized sorbent.

7. A process as in claim 1 wherein said feed contains olefins.

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## **Related Proceedings Appendix**

None.